# REMOVAL OF BORON FROM AQUEOUS SOLUTIONS BY ADSORPTION USING NATURAL ADSORBENTS

by

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## ABSTRACT

Removal of boron ions from boron containing aqueous solutions using lignite, natural zeolite (clinoptilolite) and fly ash adsorbents was studied. This study demonstrated that boron removal was controlled by the material type and operational conditions (pH, amount of the adsorbent, adsorption time, temperature). The experiments show that a considerable amount of boron (>90 %) can be removed from water with fly ash under suitable conditions of pH 10, adsorbent amount of 100 g/L, for an adsorption time of 24 hours at 25 $^{o}$C. Percentage of boron removed by zeolite and demineralized coal remained at less than 20 under the same conditions.

Freundlich, Langmuir and Dubinin-Radushkevich isotherms for the adsorbents were obtained. The adsorption of boron on demineralized lignite fitted to Langmuir isotherm, whereas adsorption on zeolite was explained by Freundlich isotherm. The adsorption on fly ash was considered to fit both Langmuir and Freundlich isotherms.

Dubinin-Radushkevich model was used to calculate adsorption energies (E) and for thermodynamic and kinetic analysis. Since E values are less than 8 kJ/mol, the type of adsorption resembles physical adsorption due to weak van der Waals forces. $\Delta G^{o}$ of adsorption of boron on fly ash was found between 3 and 4.5 kJ/mol for different temperatures. The $\Delta S^{o}$ and $\Delta H^{o}$ values of the adsorption were 0,03 kJ/molK and 13,61 kJ/mol, respectively. To analyze the adsorption kinetically, three models were considered. The pseudo-second-order model was determined to be the most suitable for adsorption on fly ash, whereas the affect of intraparticle diffusion is also considered as significant.



Key words: Boron, boric acid, borate ion, fly ash, lignite, zeolite, adsorption

# ÖZET

Bor içeren sulu çözeltilerden bor iyonlarının adsorpsiyon yöntemiyle, doğal adsorbentler kullanılarak uzaklaştırılması konusunda çalışılmıştır. Adsorpsiyon kapasitesini etkileyen faktörler: adsorbent çeşidi, pH, adsorpsiyon süresi, çözeltideki adsorbent miktarı ve sıcaklık olarak belirlenmiştir. Yapılan deneylerde, adsorbent olarak uçucu kül kullanıldığında ve optimum şartlar sağlandığında (25 $^{o}$C, pH 10, 100 mg/L adsorbent, 24 saat karışma süresi) çözeltideki bor miktarında % 90 ın üzerinde azalma gözlenmiştir. Bunun yanında, aynı şartlarda linyit ve doğal zeolitin (klinoptilolit) adsorpsiyon özellikleri incelendiğinde, bu malzemeler için bor konsantrasyonundaki azalmanın % 20 yi geçmediği gözlenmiştir.

Değişik başlangıç konsantrasyonlarıyla deneyler yapılarak, elde edilen sonuçlarla Langmuir, Freundlich ve Dubinin-Radushkevich izotermleri çizilmiştir. Borun doğal zeolit kullanılarak adsorbe edilmesinde en uygun izoterm Freundlich olarak belirlenirken, linyit icin adsorpsiyon özelliğinin Langmuir izotermine daha uygun olduğu gözlenmiştir. Bununla beraber, uçucu kül için Langmuir ve Freundlich izotermlerinin doğrusallığı birbirine çok yakın olduğundan, bu adsorbent için Freundlich izotermi de göz önünde bulundurulmalıdır.

Dubinin-Radushkevich izotermleri kullanılarak adsorpsiyon enerjileri (E) hesaplanmış ve borun uçucu kül ile adsorpsiyonu termodinamik ve kinetik açıdan incelenmiştir. Uçucu kül için adsorpsiyon enerjileri 8 kJ/mol den küçük değerler olarak hesaplandığından, adsorpsiyonun çeşidi Van der Waals kuvvetlerine bağlı fiziksel adsorpsiyon olarak belirlenmiştir. Farklı sıcaklıklardaki adsorpsiyonlar için $\Delta G^{o}$ değerleri 3 ve 4.5 kJ/mol arasında hesaplanmıştır. Adsorpsiyon için $\Delta S^{o}$ ve $\Delta H^{o}$ değerleri sırasıyla 0,03 kJ/molK and 13,61 kJ/mol olarak elde edilmiştir. Adsorpsiyonu kinetik açıdan incelemek için üç model incelenmiştir. Yalancı (pseudo) ikinci derece modeli borun kül ile adsorpsiyonu için en uygun yaklaşım olarak belirlenmekle beraber, parçacık içi difüzyon modelinin de adsorpsiyonda etkin olduğu söylenebilir.

Anahtar kelimeler : Bor, borik asit, borat, uçucu kül, linyit, zeolit, adsorpsiyon

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**TABLE OF CONTENTS** **Page**

## LIST OF FIGURES AND TABLES

**FIGURES** **Page**

**TABLES**

## NOMENCLATURE

$C_e$ : Equilibrium solution concentration (mmol/L)

$C_s$ : Amount adsorbed on solid (mmol/g)

$C_m$ Maximum adsorption capacity (mmol/g)

E : Mean free energy of adsorption (kJ/mol)

$k_1$ : Pseudo-first order rate constant ($h^{-1}$)

$k_2$ : Pseudo-second order rate constant ($h^{-1}$)

$K_c$ : Adsorption equilibrium constant

L : Liquid flow rate ( kmol/h)

q : The amount of boron adsorbed (mg/g)

t : time

V : Vapor flow rate, kmol/h

x : Mole fraction in liquid

y : Mole fraction in vapor

Greek Letters

$\Delta G$ : change in Gibbs free energy

$\Delta H$ : change in enthalpy

$\Delta S$ : change in entropy

# CHAPTER 1

# INTRODUCTION

Boron is a naturally occurring element, which is found in nature combined with oxygen and other natural elements forming several different minerals called borates. Borate minerals are present in the oceans, sedimentary rocks, coal, shale and some soils. The average concentration of boron in rocks varies from 5 mg/kg to 100 mg/kg, whereas in the ocean, the boron concentration is approximately 4.5 mg/L. Boric acid and many borates are soluble in water (5.7 g boric acid/100 ml water at 25°C) and in biological fluids such as saliva and blood.

The primary source of boron is the mining of boron-containing minerals such as colemanite, ulexite, tincal, and kernite. These minerals are located in various regions of Turkey, USA, and also in Argentina, Chile, Russia, China, and Peru. Among them, Turkey can be considered to have one of the largest natural reserves of boron, possessing approximately 60% of the world's reserves [1]. The borate reserves in Turkey are located mainly in four districts: Emet, Bigadiç, Kırka and Mustafakemalpaşa (Kestelek) [2, 3].

Boron is a significant industrial material, which is used in the production of glass, textiles, fiberglass, disinfectants, cosmetics, cleaning and bleaching agents, wood preserving materials, fire retardant materials, plastics, ceramics, food preservatives, synthetic rocket fuels, abrasives, absorption units in nuclear reactors, medicines, insecticides, cancer therapy drugs, and agricultural fertilizers [4].

Being a useful element, it is known that boron is harmful to the environment when it exists at elevated concentrations in soil and water. Boron is known as an essential micronutrient for plants, which can be toxic to plants at high concentrations. Thus, boron compounds cause

some serious health and environmental problems, when its complexes pass to groundwater [5]. Boron (III) has toxicity for reproduction and causes disease of the nervous system [6]. In arid regions, additions of boron with irrigation water often lead to toxicity symptoms and reduce plant yields [7]. Knowing these facts, boron must be removed from water and wastewater. A concentration in excess of 2.0 mg/L in irrigation water is deleterious to certain plants and some plants can also be affected by concentrations as low as 1.0 mg/L [8].

There are several batch and column methods to remove boron from waste water. These methods can be summarized as: Adsorption on some synthetic and natural microporous materials, ion-exchange resins and cross-linked polymer gels. Batch adsorption is considered as one of the most efficient methods. Adsorbents used for this purpose are natural and synthetic zeolites, $Al_2O_3$ based materials, modified zeotype materials, activated carbons etc. These adsorbents can adsorb up to 80 – 90 % of B ions in aqueous solutions. When large quantities of water are to be treated, cost of these adsorbents becomes an important factor for the economy of the process. To overcome this disadvantage, lower-cost, natural microporous materials can be used as adsorbents. Some examples of these natural materials are fly ash, natural zeolites, coal, lignite, clay, sawdust and so on.

The aim of this study was to utilize natural adsorbents to remove boron ions from aqueous solutions. In the present study lignite, demineralized lignite, natural zeolite (clinoptilolite) and fly ash were used as adsorbents for the removal of boron, and the adsorption properties of these materials were investigated. Time of adsorption, adsorbent dose, initial boron concentration, pH and temperature were the parameters studied to analyze the adsorption characteristics of the adsorbents. The results of adsorption experiments were analyzed by Langmuir, Freundlich and Dubinin-Radushkevich models. Since fly ash was determined to be the most efficient adsorbent, results of experiments done with this at different temperatures were used to calculate some thermodynamic and kinetic parameters.

# CHAPTER 2

# BACKGROUND

## 2.1. Theory

### 2.1.1. Adsorption

As a general definition, adsorption is a process that occurs when one or more components of a gas or a liquid stream accumulate on the surface of a solid adsorbent, and separation is achieved. During the process, the gas or solute forms a film of molecules or atoms (the adsorbate) on the surface of the adsorbent. It is different from absorption, in which a substance diffuses into a liquid to form a solution. The term sorption encompasses both processes, while desorption is the reverse process.

There are different types of adsorption such as: physisorption, chemisorption and biosorption. Physisorption or physical adsorption is a type of adsorption, in which the adsorbate adheres to the surface only through weak intermolecular interactions (van der Waals). It is characterized by low ambient temperature (always under the critical temperature of the adsorbate) and low enthalpy ($\Delta H < 20$ kJ/mol). In physisorption, adsorption takes place in multilayers. The process requires low activation energy and the energy state of adsorbate is not altered. Physisorption is a reversible process.

Chemisorption is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond, as opposed to the Van der Waals forces which cause physisorption. It is characterized by high temperatures and high enthalpy (50 kJ/mol $<\Delta H<$ 800 kJ/mol). The strength of the interaction is stronger than pure physical adsorption, and more likely there is a chemical (covalent) bond between adsorbate and surface. Bond strength

of around 80 kJ/mol is often taken to be indicative of a true chemical interaction. In chemisorption, adsorption takes place only in a monolayer. The process has high activation energy and there is an increase in electron density in the adsorbent-adsorbate interface. Chemisorption is reversible only at high temperature.

Biosorption is the binding and concentration of heavy metals from aqueous solutions (even very dilute ones) by certain types of inactive, dead, microbial biomass. Biomass exhibits this property, acting just as a chemical substance, as an ion exchanger of biological origin. It is particularly the cell wall structure of certain algae, fungi and bacteria which was found responsible for this phenomenon. Bioaccumulation is the opposite of biosorption, which is metabolically driven active by living cells.

Adsorption can be performed both in batch and column processes. A schematic representation of an adsorption column is given in Figure 2.1 L and V represents the liquid and gas amounts respectively whereas x and y represents the liquid and gas concentrations.

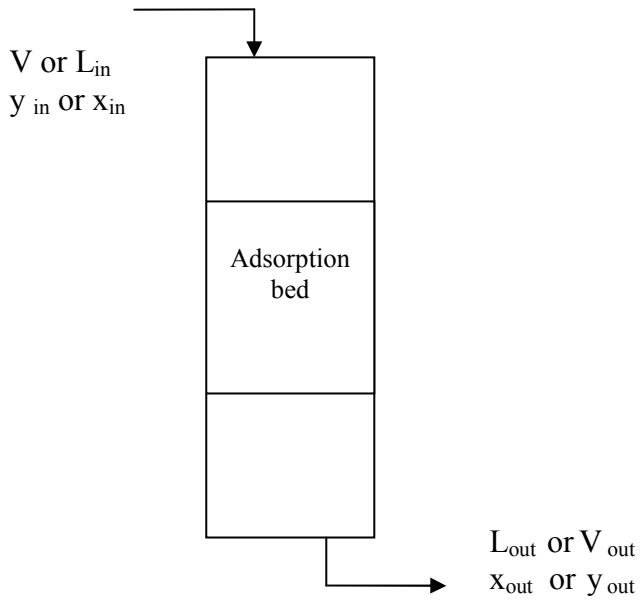


**Figure 2.1.** Schematic representation of an adsorption tower.

**Batch Adsorption**

Batch adsorption is often used to adsorb solutes from liquid solutions. This method is used generally when a small amount of liquid is treated (for example: pharmaceutical industry). The material balance of the batch adsorption can be summarized as follows:

$$q_F M + c_F S = qM + cS \quad (1)$$

Where, M is the amount of adsorbent and S is the volume of the feed solution. The initial feed concentration is $c_{F,}$ the final equilibrium concentration is c; and the initial concentration of the adsorbed solute is $q_F$ and the final equilibrium value is q [9].

**2.1.2. Adsorbents**

**Physical properties of adsorbents:**

There are a large number of adsorbents developed for a number of separation processes. Generally, the adsorbents are in the form of pellets, beads or granules. The main characteristic of an efficient adsorbent is its porous structure (with pore volumes up to 50 % of the total particle volume).

Usually, the adsorption occurs as a monolayer on the surface of the fine pores. However, sometimes several layers may occur. Physical (van der Waals) adsorption generally occurs between the adsorbed molecule and the solid internal pore surface and is reversible.

The overall adsorption process consists of a series of steps. When the fluid is flowing over the particles in the fixed bed, the solute first diffuses from the bulk fluid to the gross exterior surface of the particle. Then it diffuses into the pore and the solute is adsorbed on the surface. Various commercial adsorbents with large pore surface areas (100 – 2000 $m^2/g$) can be summarized as follows [9]:

a. **Activated carbon:** Activated carbon, which is one of the most efficient and widely used adsorbents, is a microcrystalline material made by thermal decomposition of wood, vegetable shells, coal and so on. The surface area of this material can vary from 300 to 1200 $m^2/g$ with average pore diameters of 10-60 Å.

b. **Silica Gel:** Silica gel adsorbent is made by acid treatment of sodium silicate solution and drying. The surface area is generally between 600 and 800 $m^2/g$ and average pore diameter differs between 20 to 140 Å.

c. **Activated alumina:** This adsorbent is prepared by activating hydrated aluminum oxide by heating to remove water. Surface area range of this material is 200 - 500 $m^2/g$ and the pore diameters are between 20 and 140 Å.

d. **Molecular Sieve Zeolites:** The zeolites, which will be considered in detail in the next section, are porous crystalline aluminasilicates that form an open crystal lattice containing uniform pores. This property makes zeolites different from other adsorbents which have a range of pore sizes. Different zeolites have pore sizes about 3-10 Å.

e. **Synthetic Polymers or Resins:** These adsorbents are made by polymerizing two major types of monomers. The polymers made from aromatics (ex: styrene and divinylbenzene) are used to adsorb nonpolar organics from aqueous solutions, whereas those made from acrylic esters are used to adsorb more polar solutes in aqueous solutions.

**Natural Adsorbents Used for Water Treatment**

Considering the adsorbents used in water treatment processes, activated carbon has been the most popular and widely used adsorbent [12]. On the other hand, activated carbon is an expensive material. Activated carbon also requires complexing agents to improve its removal performance for inorganic matter, and this situation makes it no longer attractive to be widely used in small-scale industries because of cost inefficiency [12]. Therefore, scientists tend to

do research about low-cost natural adsorbents for water treatment. Some examples of these natural adsorbents are natural zeolites, lignite, fly ash, chitosan, clay, peat moss, xanthate, rice husk carbon (RHC), coconut shells, and so on.

### a. Natural Zeolite

Millions of years ago, zeolite deposits formed when volcanoes erupted enormous amounts of ash–aluminosilicates of alkali and alkaline earths. Some of the wind borne ash settled to form thick ash beds. In some cases the ash fell into lakes and in others, water percolated through the ash beds. In all cases, the chemical reaction of volcanic ash and salt water resulted in the formation of natural zeolites.

Natural zeolites (i.e. zeolite minerals), are mainly called hydrated sodium potassium calcium aluminum silicates. The zeolite minerals are composed of aluminosilicates with a three dimensional framework structure bearing $AlO_4$ and $SiO_4$ tetrahedra [11] (the general formula is: $(Na,K,Ca)_{2\text{-}3}.Al_3(Al,Si)_2Si_{13}.O_{36}.12H_2O$). These molecules are linked to each other by sharing all of the oxygen to form interconnected cages and channels (Figures 2.2, 2.3). The structures contain mobile water molecules and alkali (Na, K, Li, and Cs) and/or alkaline earth (Ca, Sr, Ba, and Mg) cations. The exchangeable cations give rise to the ion exchange properties of the material. Only a few of the existing natural zeolites in the world are found in sufficient quantity and purity as required by industry. Silica-rich heulandite (clinoptilolite) and mordenite are the most important natural zeolites and they play a significant industrial role. Some major uses of zeolite minerals are water softening, gas and petroleum processing, mining, sewage treatment, paper products and so on [11].

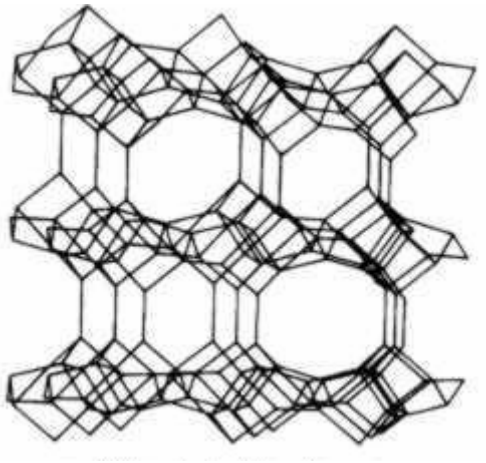

**Figure 2.2.** The structure of clinoptilolite

In view of the porous structure of zeolites, it is known that they have a considerable adsorption capacity [12, 13]. It is also known that synthetic zeolites, like zeolite-X and zeolite-A can be effectively used in water treatment processes [14, 15]. On the other hand, although some impurities and some defects of crystals decrease the efficiency, natural zeolites are also useful adsorbents.

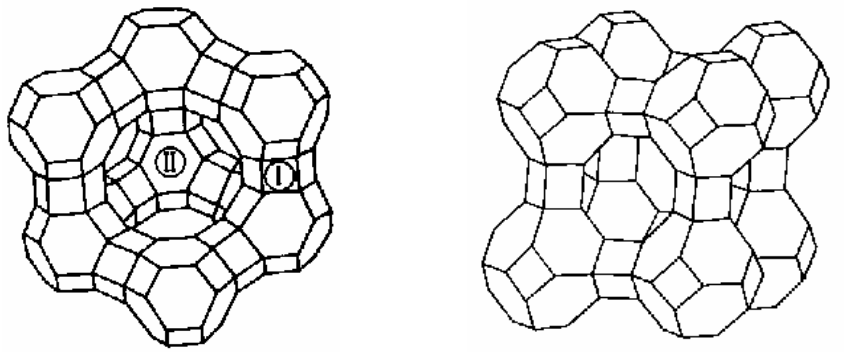


**Figure 2.3.** The structures of Zeolite-X and Zeolite-A respectively

**b. Fly Ash**

Fly ash closely resembles volcanic ashes used in production of the earliest known hydraulic cements about 2,300 years ago. Those cements were made near the small Italian town of Pozzuoli - which later gave its name to the term "pozzolan".

Instead of volcanoes, today's fly ash comes primarily from coal-fired power plants generating electricity. These power plants grind coal to powder fineness before it is burned. Fly ash - the mineral residue produced by burning coal - is captured from the power plant's exhaust gases and collected for use [16]. Fly ash can be defined as the non-combustible residue that results from burning fuels (ex: coal) in an incinerator, boiler or furnace. It can include metal oxides, silicates, and sulfur compounds. Fly ash is generally captured from the chimneys of power generation facilities, whereas bottom ash is removed from the bottom of the furnace.

In the past, fly ash was generally released into the atmosphere via the smoke stack, but pollution control equipment mandated in recent decades now require that it be captured prior to release. Fly ash particles are suspended in the exhaust gases and are collected by electrostatic precipitators or filter bags. The fly ash particles suspended in the exhaust gases, are generally spherical in shape and range in size from 0.5 μm to 100 μm.

Depending upon the source and makeup of the coal being burned, the components of the fly ash produced vary considerably, but all fly ash includes substantial amounts of silica (silicon dioxide, $SiO_2$) (both amorphous and crystalline) and lime (calcium oxide, CaO). They consist mostly of silicon dioxide ($SiO_2$), which is present in two forms: amorphous, which is rounded and smooth, and crystalline, that is sharp, pointed and hazardous; aluminum oxide ($Al_2O_3$) and iron oxide ($Fe_2O_3$). Fly ashes are generally highly heterogeneous, consisting of a mixture of glassy particles with various identifiable crystalline phases such as quartz, mullite, and various iron oxides.

Two classes of fly ash are defined by ASTM C618 (Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete): Class F fly ash and Class C fly ash. The chief difference between these classes is the amount of calcium, silica, alumina, and

iron content in the ash. The chemical properties of the fly ash are largely influenced by the chemical content of the coal burned (i.e., anthracite, bituminous, and lignite).

When you burn massive amounts of pulverized coal, one of the waste products is an ash that acts a lot like cement in the right recipe [17]. That makes for a great relationship between coal-fired power plants and ready-mix concrete producers who use fly ash as an admixture.

Ash used as a cement replacement must meet strict construction standards. 75% of the ash must have a fineness of 45 μm or less, and have carbon content, measured by the loss on ignition (LOI), of less than 4%. In the U.S., LOI needs to be fewer than 6%.
The particle size distribution of raw fly ash is very often fluctuating constantly, due to changing performance of the coal mills and the boiler performance.

Considering the porous structure of fly ash particles, fly ash can be stated as a natural adsorbent for several adsorption processes. In water treatment processes, to remove heavy metal ions and boron ion from waste water, fly ash is one of the most popular natural adsorbents because of its low cost and large availability (because it is a waste product of coal-fired electricity generating power plants).

### c. Coal and Lignite

Coal, a naturally occurring combustible solid, is one of the worlds most important and abundant energy sources. From its introduction 4,000 years ago as a fuel for heating and cooking, to its nineteenth- and twentieth-century use in thermal power plants to generate electricity and as a chemical feedstock, coal, along with oil and natural gas, has remained an important source of energy [18]. The complex structure of coal is presented in Figure 2.4.

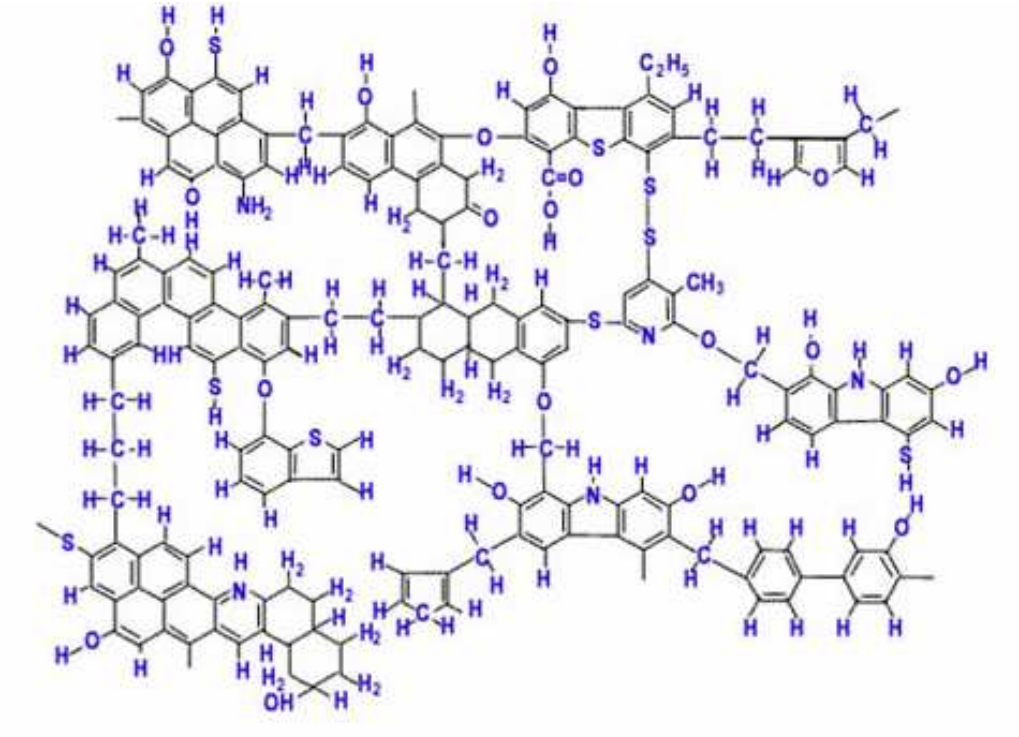

**Figure 2.4.** The complex structure of bituminous coal [19]

Lignite, often referred to as brown coal, is the lowest rank of coal and used almost exclusively as fuel for thermal steam-electric power generation. It is brownish-black and has a high inherent moisture content compared with bituminous coal. It is also a heterogeneous mixture of compounds for which no single structural formula will suffice.

The heat content of lignite ranges from 10 to 20 MJ/kg on a moist, mineral-matter-free basis. The heat content of lignite consumed in the United States averages 15 MJ/kg, on the as-received basis (i.e., containing both inherent moisture and mineral matter).
When lignite is reacted with quaternary amine, amine treated lignite (ATL) forms. ATL is used in drilling mud to reduce fluid loss.

Because of its low energy density, brown coal is inefficient to transport and is not traded extensively on the world market compared with higher coal grades. It is often burned in power stations constructed very close to any mines, such as in Yatagan and Kemerkoy, Mugla, Beypazari, Ankara and Australia's Latrobe Valley and Luminant's Monticello plant in Texas. Carbon dioxide emissions from brown coal fired plants are generally much higher than for comparable black coal plants. The continued operation of brown coal plants, particularly

in combination with strip mining and in the absence of emissions-avoiding technology like carbon sequestration, is politically contentious [20].

Lignite can be separated into two types. The first is xyloid lignite or fossil wood and the second form is the compact lignite or perfect lignite.

Although the xyloid lignite may sometimes have the tenacity and the appearance of ordinary wood it can be seen that the combustible woody tissue has experienced a great modification. It is reducible to a fine powder by trituration and if submitted to the action of a weak solution of potash it yields a considerable quantity of humic acid [21].

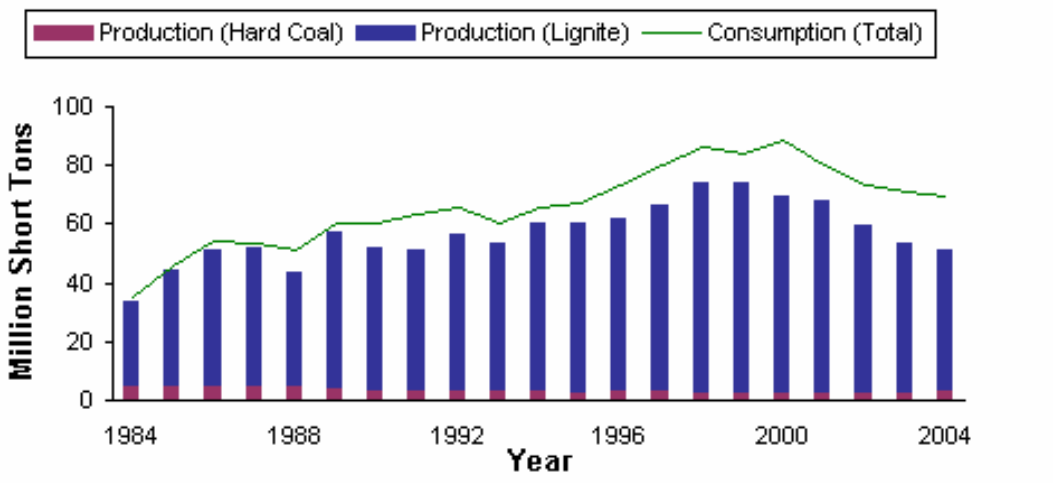


**Figure 2.5.** Turkey's coal production and consumption, 1984-2004 [22]

### 2.1.3. Adsorption Isotherms

Adsorption isotherms are the linearized equations which give information about the characteristics of adsorption processes. There are several isotherms defined, such as Langmuir isotherm, Freundlich isotherm and Dubinin-Radushkevich isotherm. Once the plots are obtained according to isotherm equations and experimental data, it can be determined, which isotherm most fits to the characteristic of the adsorption.

Langmuir equation can be applied to obtain monolayer capacity and is represented as:

$$C_e / C_s = 1 / C_m L + C_e / C_m \quad (2)$$

Where, $C_s$ is the amount adsorbed on solid (mmol/g), $C_e$ is the equilibrium solution concentration (mmol/L), $C_m$ is adsorption capacity (maximum amount that can be adsorbed by adsorbent as monolayer (mmol/g), and L is a constant related to the adsorption energy.

Freundlich isotherm is not restricted to the formation of the monolayer coverage and it assumes that adsorption occurs on heterogeneous surface of solid. Freundlich equation can be applied to quantify relative adsorption capacity and the relation can be given as,

$$C_s = K_f C_e^{\,n} \quad (3)$$

Where, $C_s$ is the amount of adsorbed of solute (mmol/g); $C_e$ is equilibrium solution concentration of solute (mmol/L); $K_f$, (mmol/g) can be considered as a measurement of the relative adsorption capacity since it is the value of $C_s$, when $C_e$ is unity [23]; $n_f$ is a constant representing the adsorption intensity of the adsorbent. A linear form of the Freundlich equation can be found by taking logarithms of the equation,

$$\ln C_s = \ln K_f + n_f \ln C_e \quad (4)$$

$K_f$ and $n_f$ values are obtained by plotting ln $C_e$ versus ln$C_s$. Due to inherent bias resulting from linearization, the alternative isotherm parameters were determined by nonlinear regression through the Freundlich equation.

It is known that Langmuir and Freundlich isotherms may not always give enough information about the adsorption type. In order to clarify the adsorption type, equilibrium data should also be applied to Dubinin-Radushkevich (DR) isotherm with the following equation [24].

$$\ln C_s = \ln X_m - k\varepsilon^2 \quad (5)$$

where ε is Polanyi potential (RT ln(1+1/$C_e$)), $C_s$ is the amount of adsorbate adsorbed per unit weight of adsorbent (mol/g), $C_e$ is the equilibrium concentration of boron (mol/L), $X_m$ is the adsorption capacity (mol/g), k is a constant related to adsorption energy ($mol^2/kJ^2$), T is the temperature (K), and R is the gas constant (kJ/molK). $X_m$ and k values can be obtained by plotting ln$C_s$ versus $\varepsilon^2$ at various temperatures. The slope of line yields k ($mol^2/kJ^2$) and the intercept is equal to ln$X_m$.

The mean free energy of adsorption (the free energy change when one mol adsorbate is transferred from infinity in solution to the surface of the adsorbent) was obtained from the following relationship

$$E = -(2k)^{-0.5} \quad [25\text{-}28] \quad (6)$$

If E is less than 8 kJ/mol, it can be said that the adsorption is physical adsorption due to weak van der Waals forces [29,30]

### 2.1.4. Thermodynamics of adsorption

Thermodynamics can be defined as a branch of physical chemistry which is concerned with the study of the transformations of energy [31]. The important expressions used in thermodynamics are mainly work, heat, enthalpy, internal energy, entropy and Gibb's free energy.

Work (W) is the motion against an opposing force whereas energy is the capacity to do work. Heat (Q) is energy transferred from one body or system to another due to a difference in temperature [32]. Internal energy (U) of a system is the sum of all kinetic and potential contributions to the energy of all atoms, ions and molecules of the system. It is an extensive property and it generally depends on temperature and pressure.

Internal energy change of a system can be expressed as follows in a very general equation:

$$\Delta U = Q + W \tag{7}$$

Enthalpy can be defined with the following equation:

$$H = U + PV \tag{8}$$

Enthalpy differs from the internal energy by addition of the product of the pressure (P) and the volume (V) of the system. The measure of disorder of a system used in thermodynamics is called the entropy (S). According to second law of thermodynamics, the entropy of an isolated system tends to increase.

Gibb's free energy (G) is a kind of energy of a system, which gives us an opinion whether a process is spontaneous or not. Every system tends to have the minimum energy to be stable. The general equation of Gibb's free energy is

$$G = H - TS \tag{9}$$

At constant temperature, the change in Gibb's free energy is:

$$\Delta G = \Delta H - T\Delta S \quad (10)$$

For all, S, H and G, the difference in these parameters between the products and reactants in their standard states are called standard entropy ($S^0$), standard enthalpy ($H^0$) and standard Gibb's free energy ($G^0$) respectively.

In order to understand the effect of temperature on the adsorption process, thermodynamic parameters should be determined at various temperatures. The molar free energy change of the adsorption process is related to the equilibrium constant ($K_c$) and calculated from the equation:

$$\Delta G^0 = -RT \ln K_c \quad (11)$$

Where, R is the gas constant (8.314 J/mol K), T is the absolute temperature. $K_c$ values can be estimated as:

$$K_c = C_s/C_e \quad (12)$$

Where $C_s$ is the equilibrium concentration of boron on adsorbent (mmol/g), $C_e$ is the equilibrium concentration of boron in the solution (mmol/L). Standard enthalpy change, $\Delta H^0$, and standard entropy change, $\Delta S^0$, of adsorption can be estimated using the following equation:

$$\ln Kc = -\Delta H^0_{ads}/RT + \Delta S^0/R. \quad (13)$$

Looking at the equation given above, a plot of $\ln K_c$ against 1/T renders a straight line. The slope of that straight line is equal to $-\Delta H^0/R$ and its intercept value is equal to $\Delta S^0/R$.

### 2.1.5. Kinetics of Adsorption

Reaction kinetics is the study of rates of chemical processes. Chemical kinetics includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction.

Using the adsorption time and the amount of adsorbed boron data, the kinetic parameters of adsorption can be calculated. There are several kinetic models that can be applied to estimate the adsorption mechanism of boron onto fly ash. Three of these models are: pseudo-first-order, the pseudo-second-order, and the intraparticle diffusion model [33], the equations of which are presented below, respectively.

$$1/q = (k_1/q_1)(1/t) + 1/q_1 \quad (14)$$

$$t/q = (1/k_2q_2^2) + t/q_2^2 \quad (15)$$

$$q = k_p t^{1/2} + C \quad (16)$$

Where, q is the amount of boron adsorbed (mg/g) at time t, $q_1$ is the maximum adsorption capacity (mg/g) for pseudo first-order adsorption, $k_1$ is the pseudo-first-order rate constant for the boron adsorption process ($h^{-1}$), $q_2$ is the maximum adsorption capacity for the pseudo second order adsorption (g/mg h), $k_2$ is the pseudo second order rate constant ($h^{-1}$), $k_p$ is the intraparticle diffusion rate constant ($mg/gh^{1/2}$), and C is the intercept. These parameters can be estimated with the help of some plots.

For the pseudo first order model, the $1/q_t$ versus 1/t should give a straight line. The slope of this plot gives $k_1/q_1$ and the intercept is $1/q_1$. For the pseudo second order model the linear plot should be t/q versus t, the slope of which is $1/q_2^2$ and the intercept of which is $1/k_2q_2^2$. For the last model, intraparticle diffusion, the plot of $q_t$ versus $t^{1/2}$ should give a line. The slope of this line gives $k_p$ and the intercept is C.

## 2.2. Literature Survey

The U.S. Bureau of Mines and U.S. Geological Survey, report that world production of borate minerals and boron chemical derivatives are about $5\times10^6$ tons of $B_2O_3$ per year and world reserves are calculated as $270\times10^6$ tons (in $B_2O_3$ form). The United States (42%), Turkey (42%) and South America (11%) are the biggest producers and they constitute about 95% of borate production worldwide [34]. The occurrence of boron compounds in waters increases in a continuous and parallel way to industrial development. The main boron sources, whose presence is detected in surface waters, are urban wastes rich in detergents and cleaning products; industrial wastes, which can come from a wide range of different activities as well as several chemical products used in agriculture [35]. Boron is generally found in natural water as boric acid, $B(OH)_3$, and/or borate ion, $B(OH)_4^-$ [36].

Boron is an essential nutrient for plants, but can be toxic to organisms when accumulated in high concentrations. Boron is widely distributed in nature in low concentrations, and is usually <0.1–0.5 ppm in surface freshwaters; but its higher concentrations are measured in a few areas [36, 37]. High levels of boron concentrations in the range of 1-63 ppm causes environmental problems in ground thermal waters and surface waters in some agricultural areas of western Anatolia. Sericite, illite and tourmaline minerals, which are abundant in Menderes Massif rocks, are considered to be the main reason for the high boron contents [38]. Kizildere, which is the only commercial geothermal power plant in Turkey and located in Büyük Menderes River in south-west Turkey, discharges annually 6 million tons of wastewater into the Büyük Menderes river, creating environmental pollution. Currently, the wastewater, which includes up to 24 ppm boron, is discharged into the river at a rate of 750–1500 tons per hour [39]. Boron concentrations of 4.7 ppm in seawater, 0.5-2 ppm in domestic wastewater and up to 8 ppm in regional groundwater are measured in Italy, Cyprus and Greece. The World Health Organization defines boron level of 0.3 ppm as the non-observed effect level for drinking water [40]. In 1998 the European Union (EU) revised its Drinking Water Directive, which is responsible for regulating the quality of water in the EU intended for human consumption. Specifically, the EU added a new standard for boron in drinking water (1 ppm) and countries such as Italy and Cyprus with high natural boron concentrations in their drinking water are, thus, finding that compliance with the new EU boron regulation is more difficult and expensive than originally anticipated [41]. High boron levels in drinking

water can be toxic to humans as boron has been shown to cause male reproductive obstructions in laboratory animals [42-44].

Standard wastewater treatment methods and desalination of seawater by reverse osmosis are not successfully employed for the elimination of boron from raw waters [45]. Owing to the majority of the non-charged boric acid in the solution, only a fraction of the boron is removed during reverse osmosis desalination [47-51]. Seawater contains approximately 5 ppm of boron. In most cases, the rejection of boron by reverse osmosis is not sufficiently high, so about one third of boron content (~1.5 ppm) is normally found in permeate [52]. Therefore, seawater processed with reverse osmosis contains concentrations of boron which is above the admissible international values. The existent accepted methods for the boron removal are ion exchange by resin which involves high costs as a result of high necessity of regeneration of these resins, and physical–chemical treatments of flocculation–precipitation, also with very high costs because of the use of flocculents. The ion-exchange resin Amberlite IRA-743 is boron specific and has the capacity of almost to remove 100% of boron under high pH conditions [53-54] and has been previously used to remove boron from raw waters in Turkey [55-57].

Removing boric acid and borate ions from aqueous solutions does not seem to be straightforward, as has already been stated in the literature [58]. Conventional sedimentation and biological treatment remove insignificant amounts of boron from waters. Chemicals normally used in the water treatment industry do not have any effect on the boron levels in water. The adsorption of boron by clays, soils and other minerals has been extensively studied by many investigators [59-64]. Polat et al. [65] conducted various column and batch experiments that explored the efficiency of boron removal from seawater and desalinated seawater using several types of coal and fly ash materials under controlled conditions (pH, liquid/solid ratio, time of reaction, pre-treatment, regeneration) and reported that their experiments showed a considerable amount of boron (>90%) can be removed due to interaction with fly ash and coal under suitable conditions of high pH (>9), low liquid/solid ratio (<20), and reaction time (>6 h). A recent preliminary study [66] showed that activated alumina could be also a suitable adsorbent for the removal of boron from water. The adsorption was strongly dependent on pH, adsorbent dose and boron concentration. For initial

concentration of 5 and 50 ppm, the maximum uptake of boron reaches respectively 40% and 65% for an adsorbent dose of 0.8 and 5 g.

In the present report, removal of boron from water by adsorption using inexpensive adsorbents like fly ash, natural zeolite and demineralized lignite was investigated for the purpose of an economical water treatment process. This study showed that boron was removed with fly ash, zeolite and demineralized lignite with different capacities. Several series of batch experiments were conducted with all of the adsorbents to test the boron removal capacity and to obtain adsorption isotherms. Thermodynamic and kinetic parameters were determined for fly ash only.

# CHAPTER 3

# MATERIALS AND METHODS

## 3.1. Used Materials and Chemicals

**Chemicals:**

Boric acid ($H_3BO_3$)

Nitric acid ($HNO_3$)

Hydrochloric acid (HCl)

Hydrofluoric acid (HF)

Sodium Hydroxide (NaOH)

**Adsorbents:**

Raw lignite (obtained from Beypazari, Ankara)

Demineralized lignite

Natural zeolite (clinoptilolite, obtained from Gordes, Manisa)

Fly ash (obtained from Kemerkoy, Mugla)

## 3.2. Demineralization of Lignite

Demineralization of Beypazari lignite was performed in three steps. Before each step, lignite samples were wetted with ethyl alcohol to assure that the particles sink into the acid.

In the first step, lignite samples were treated with 5 % HCl solution at 60 $^{o}$C for 1 hour while being stirred. During this treatment, 250 ml of solution is used for each 40 g coal. After 1 hour, the lignite was filtered, washed with distilled water and dried in an oven.

Second step was HF treatment, in which 200 ml of concentrated HF is used for each 30 g of sample. The lignite was placed in a concentrated HF solution and kept at room temperature without stirring for 1 hour. In this step, it was very important to use polypropylene laboratory ware instead of glass. After the samples are filtered, washed with distilled water and dried, the third treatment was performed.

The third step involved placing the lignite in concentrated HCl at room temperature for 1 hour without stirring. After filtration, washing and drying the coal, the demineralization was completed.

To prevent the lignite from oxidizing, the samples were placed and stored in a closed container.

### 3.3. Batch adsorption

A series of batch adsorption tests were conducted to evaluate the effects of certain parameters, such as initial boron concentration, pH, amount of adsorbent and time. The adsorbents used were raw lignite, demineralized lignite, natural zeolite (clinoptilolite) and fly ash. All adsorbents were dried for 2 hours (h) before adsorption experiments. To obtain the data for different pH values, 10 mg/L boric acid solutions were prepared and the pH's were adjusted using 1M HCl and/or 1M NaOH solutions (pH values were between pH 2 and pH 11 values). For each sample, 50 ml of solution was mixed with 2 g of adsorbent and shaken in an incubator shaker (Figure 3.1) for 24 h. To determine the time required reaching equilibrium in adsorption, 10 mg/L of solution was prepared and shaken for different time intervals (between 1 hour and 26 hours). To obtain the adsorption isotherms, adsorption of boron for different initial boron concentrations was examined. Boric acid solutions corresponding to boron concentrations between 5 and 20 mg/L were prepared and shaken for 24 hours. To examine the effect of amount of adsorbent, different amounts of adsorbents between 0,5 and 2,5 g were mixed with 50 ml of 10 mg/L boron containing solutions. All these experiments were performed at 25$^{o}$C and 150 RPM mixing rate for 24 h.

To analyze the thermodynamics of adsorption of boron on fly ash samples, the batch adsorption experiments were done at two more temperatures for this adsorbent, 35 $^{o}$C and 45 $^{o}$C. These experiments were performed at pH 10, with 10 ppm initial boron concentration and 2 g of fly ash for 50 ml of boric acid solution. The adsorption time was 24 h.


**Figure 3.1.** Incubator shaker used for the batch adsorption experiments

### 3.4. Characterization

#### 3.4.1. Inductively Coupled Plasma

For each data, a sample before adsorption and a sample after adsorption were analyzed with inductively coupled plasma (ICP) to determine the initial and final concentrations. An ICP is a type of plasma source in which the energy is supplied by electrical currents which are produced by electromagnetic induction, that is, by time-varying magnetic fields.

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), also referred to as Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), is an analytical technique used for the detection of trace metals. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample.

The ICP-OES is composed of two parts: The ICP and the optical spectrometer. The ICP torch consists of 3 concentric quartz glass tubes. A water cooled coil of a radio frequency (RF) generator which surrounds part of the torch. Argon gas is typically used to create the plasma.

The equipment used in concentration analysis was: Varian, Vista-Pro CCD Simultaneous ICP-OES (Figure 3.2).


**Figure 3.2.** The ICP equipment used in the determination of the concentration of elements

### 3.4.2. X-RAY DIFFRACTION

X-ray crystallography is the science of determining the arrangement of atoms within a crystal from the manner in which a beam of X-rays is scattered from the electrons within the crystal. The method produces a graph of the density of electrons within the crystal, from which the mean atomic positions, their chemical bonds, their disorder and sundry other information can be derived.

The key step in X-ray crystallography is the diffraction of X-rays from a crystalline material. A crystal is a solid in which a particular arrangement of atoms (its unit cell) is repeated indefinitely along three principal directions known as the basis (or lattice) vectors. A wide variety of materials can form crystals (such as salts, metals, minerals, semiconductors, as well as various inorganic, organic and biological molecules), makes X-ray crystallography fundamental to many scientific fields. Although it is most informative to diffract X-rays from a single, large crystal with few defects, such crystals may be difficult to obtain; for simple

materials, it may be possible to reconstruct the atomic structure from the X-ray diffraction of polycrystalline samples, a technique known as X-ray powder diffraction.

During this research, the X-Ray diffraction results were obtained with Bruker AXS Advance D8 X-Ray diffractometer (with CuKα as the source), presented in Figure 3.3.

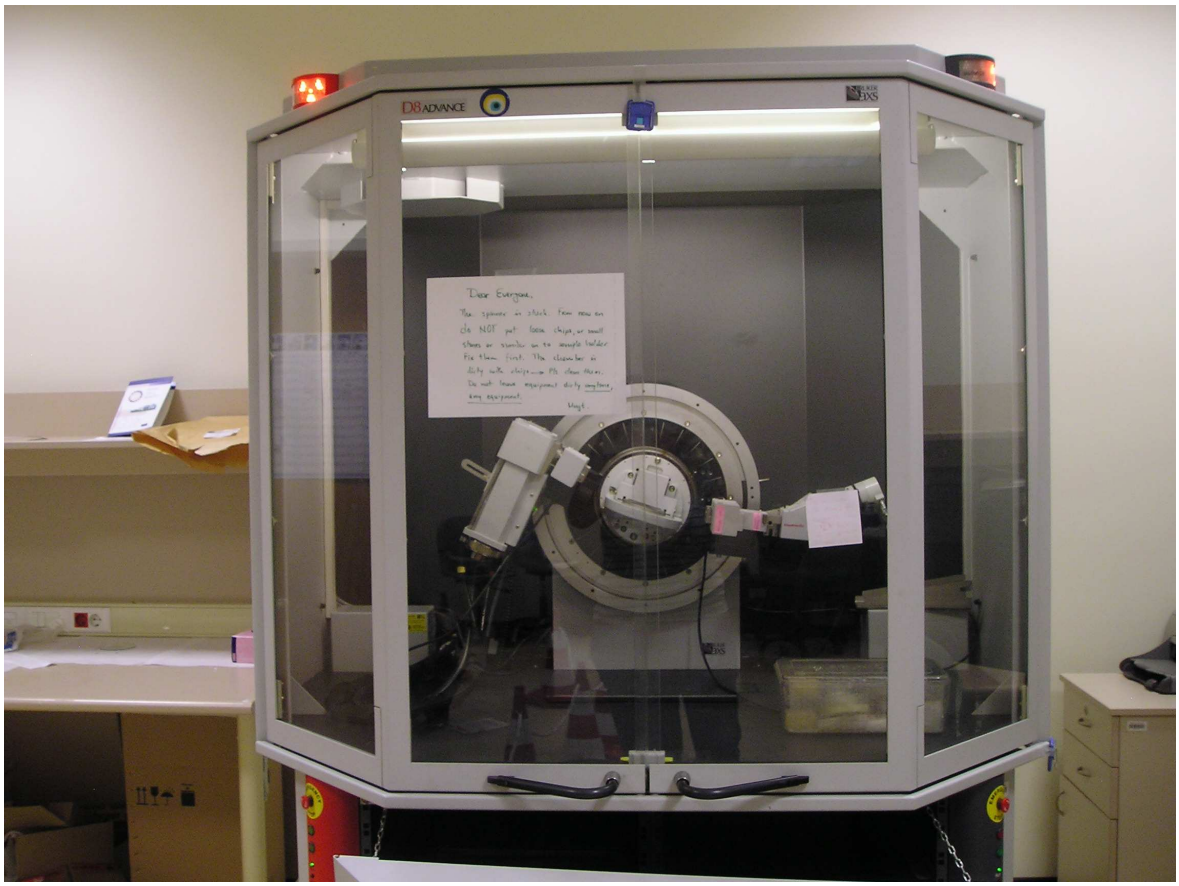


**Figure 3.3.** X-Ray diffraction equipment used in XRD analysis experiments.

### 3.4.3. Scanning Electron Microscope

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity.

During this study, the SEM pictures were taken with scanning electron microscope, Leo Supra 35 (Figure 3.4).

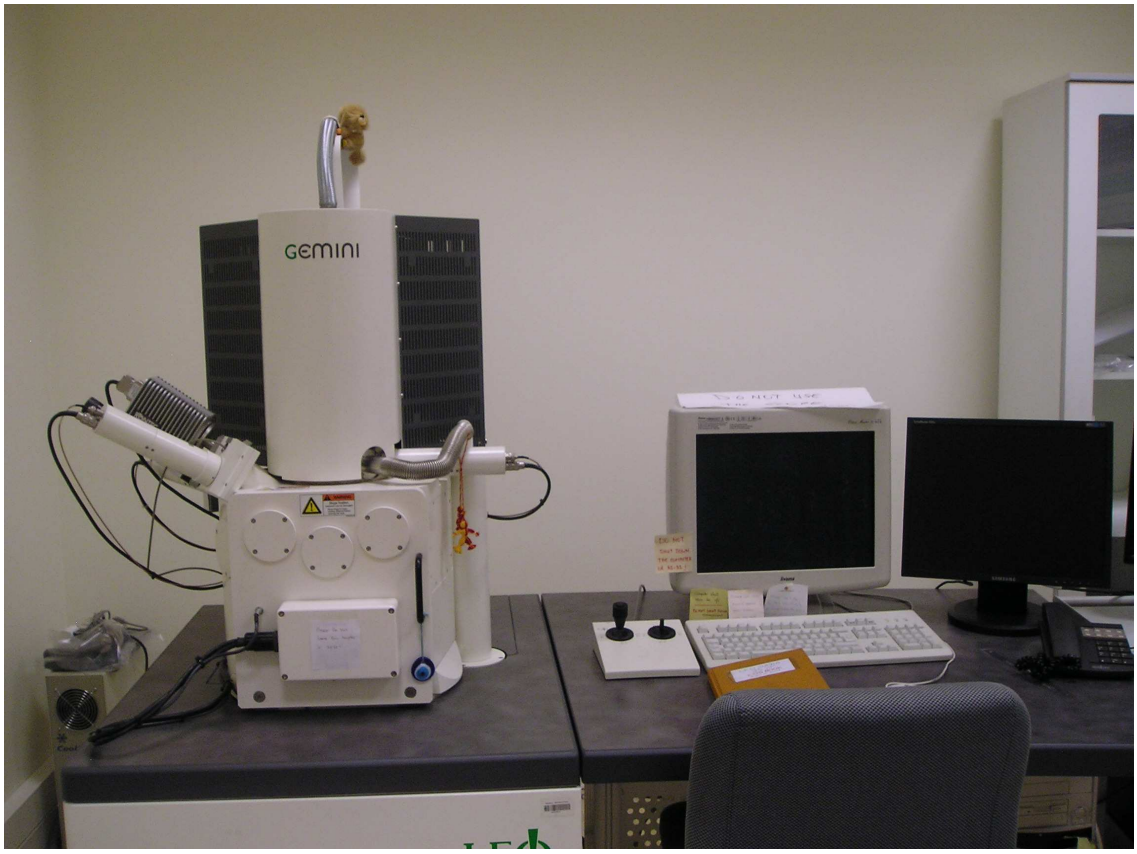


**Figure 3.4.** The Scanning Electron Microscope used to surface characterization.

### 3.4.4. BET Surface and Pore Size Analysis

BET theory is a well-known rule for the physical adsorption of gas molecules on a solid surface, that is basis for an important analysis technique for the measurement of the specific surface area of a material. In 1938, Stephen Brunauer, Paul Hugh Emmett, and Edward Teller published an article about the BET theory in a journal [40] for the first time; "BET" consists of the first initials of their family names.

The concept of the theory is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption, to multilayer adsorption with the following hypotheses: (a) gas molecules physically adsorb on a solid in layers infinitely; (b) there is no interaction between each adsorption layer; and (c) the Langmuir theory can be applied to each layer.

The BET method is widely used in surface science for the calculation of surface areas of solids by physical adsorption of gas molecules.

During this study, surface area and pore size analyses were performed with BET, NOVA 2200e Surface area and pore size analyzer (Figure 3.4). The gas sorptometer can obtain full adsorption and desorption isotherms; single point and multipoint BET surface area; Langmuir surface area; BJH adsorption and desorption, pore volume and area distributions by pore size and total pore volume.


**Figure 3.5.** BET  Surface area and pore size analyzer

# CHAPTER 4

# RESULTS AND DISCUSSION

## 4.1. Characterization

The chemical analyses of the adsorbents, Kemerköy fly ash and Gördes clinoptilolite are presented in Table 4.1.

**Table 4.1.** Chemical analyses of the Gördes zeolite and fly ash samples

| Chemical Group | Zeolite, % | Fly Ash, % |
|---|---|---|
| $SiO_2$ | 71.0 | 16.8 |
| CaO | 3.4 | 44.2 |
| $Fe_2O_3$ | 1.7 | 3.8 |
| $Al_2O_3$ | 11.8 | 9.1 |
| $K_2O$ | 2.4 | 1.4 |
| MgO | 1.4 | 2.3 |
| $Na_2O$ | 0.4 | 2.7 |
| $TiO_2$ | 0.1 | 0.5 |
| $P_2O_5$ | - | 0.2 |

To characterize the adsorbents, the XRD analyses are performed for the lignite samples before and after demineralization, and for each adsorbent, before and after batch adsorption experiments. The XRD analysis results are presented in Figures 4.1 to 4.4.

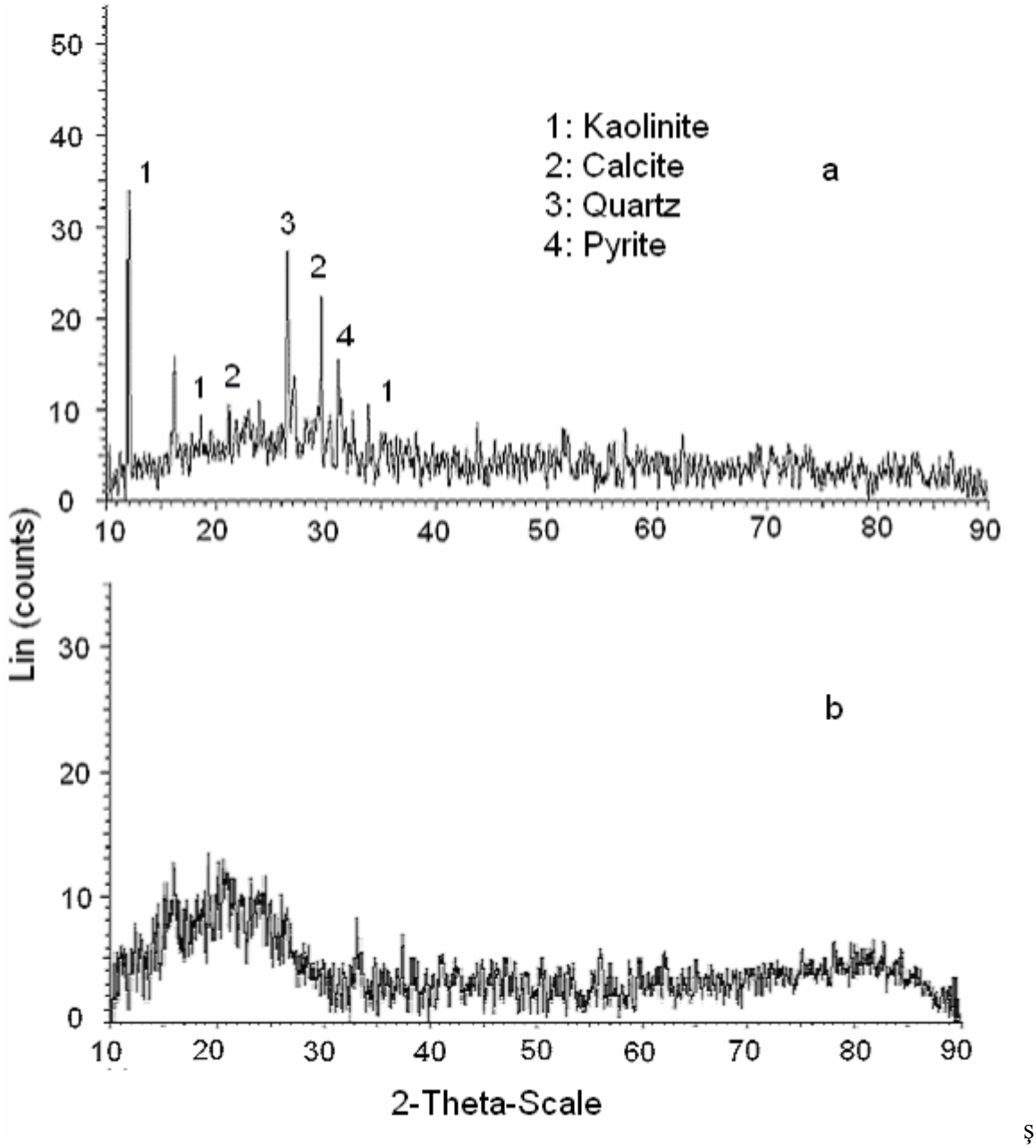


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**Figure 4.1.** XRD Results for raw lignite and demineralized lignite respectively

The results are obtained in a two-theta (2θ) scale of 10-90 and the rotation size of 20 RPM. The results presented in Figure 4.1 shows that after treating with hydrochloric, hydrofluoric acid and hydrochloric acid respectively, the peaks representing quartz, kaolinite, calcite and pyrite minerals disappeared. The XRD result for the demineralized lignite contains no sharp peaks that support the idea that all the minerals are removed from the sample.

Figure 4.2 presents the XRD results of demineralized lignite after adsorption. A sharp peak at about 26, 2θ for the sample containing adsorbed boron, does not appear in the case prior to adsorption. In literature, there are studies that indicate boron doped carbon samples give a peak at about 26 2θ [67, 68]. It is known that the boron, doped into a structure, has the ability to increase the order of the molecule. This more ordered structure means a more crystalline one and requires a sharper peak (than without B sample) in the XRD results. This effect can be the reason of observing the sharp peak at a 2θ of 26, in the results of samples with adsorbed boron.

The XRD result for zeolite (clinoptilolite) adsorbent before adsorption is presented in Figure 4.3. This result is compatible with literature. An XRD result of clinoptilolite from literature is given in the Appendix section. The powder XRD pattern of the zeolite is characterized by many peaks due its structure ordering. The XRD pattern shows sharp and symmetric peaks, which are characteristic of lamellar compounds, and also indicate a high degree of crystallinity of the zeolite sample.

The XRD result for fly ash adsorbent is given in Figure 4.4. The peaks of quartz, kaolinite and calcium oxide are observed in the XRD pattern of the fly ash sample [68].

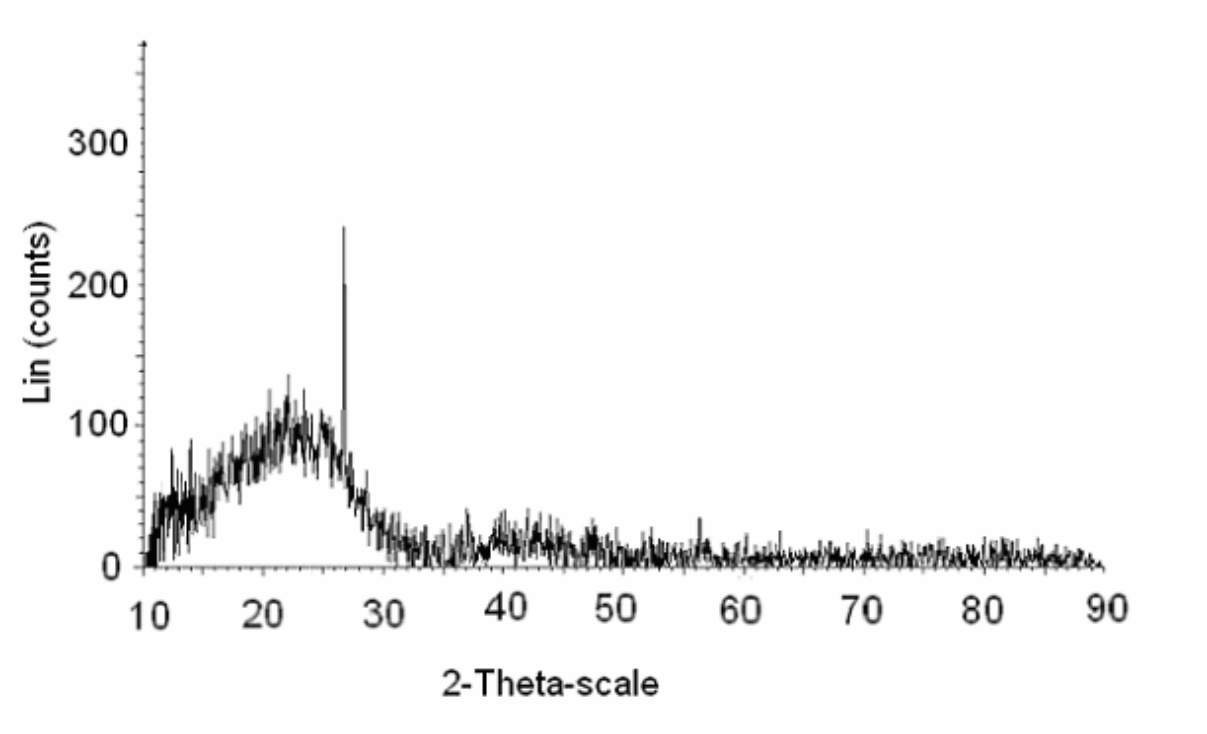



**Figure 4.2.** XRD results of demineralized lignite after boron adsorption

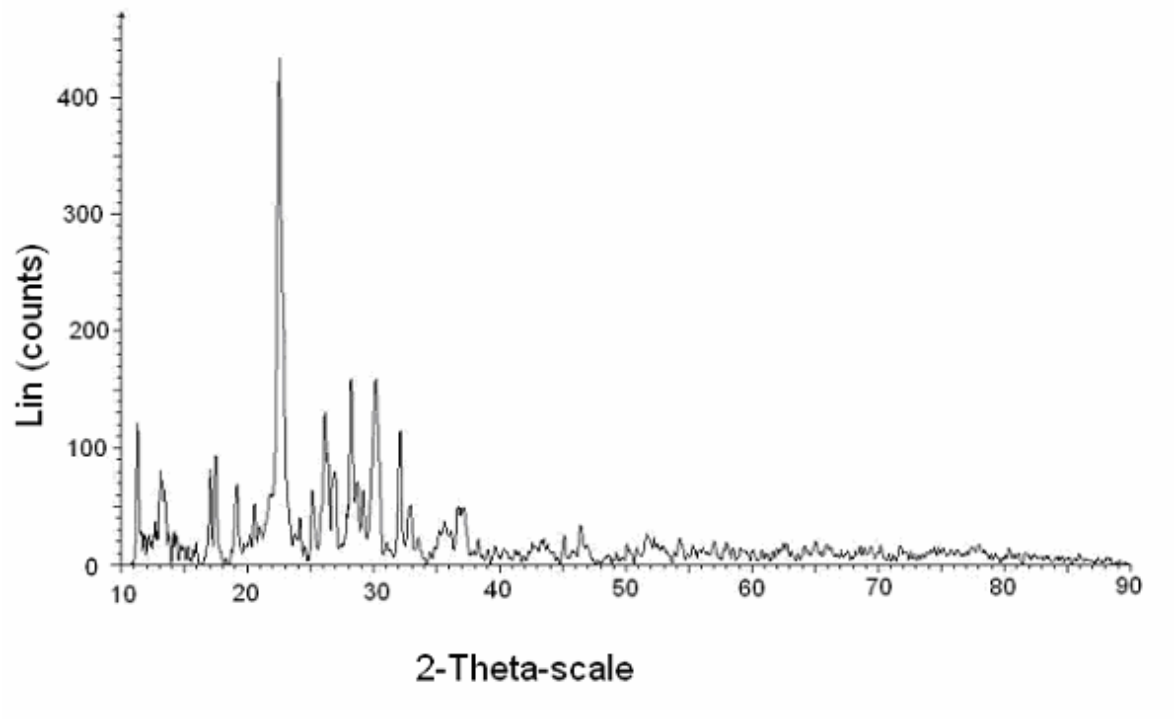



**Figure 4.3.** XRD results for clinoptilolite adsorbent

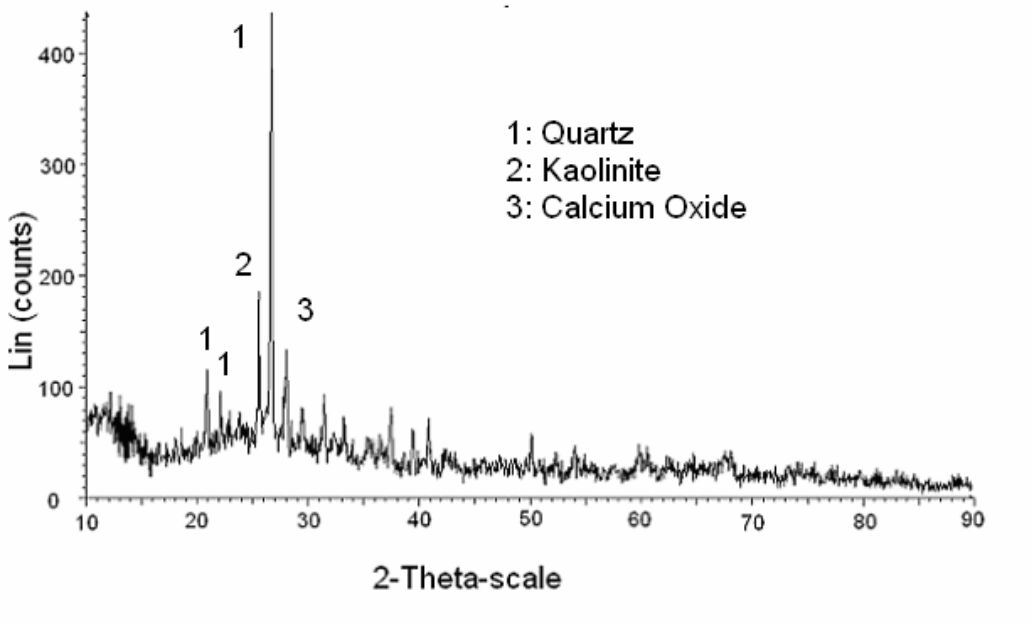



**Figure 4.4.** XRD results of fly ash adsorbents

The SEM images of the adsorbents: raw lignite, demineralized lignite, clinoptilolite and fly ash is presented in the Figures 4.5-4.8. The images are obtained at 250 X, 500 X and 20 KX magnitudes for each adsorbent respectively.

It can be observed from the images that the fly ash samples have an enhanced porous structure compared to the other adsorbents. The pores of the fly ash sample and spherical structure of particles can be observed especially for the magnitude of 20 KX for fly ash. Another SEM image for 5000 X of magnification is presented in the Appendix section, in which the porous structure of fly ash is also observed clearly.

It is known that the zeolites have also porous structure. The zeolites used are on "as received" basis during the experiments. There can be a lot of impurities in zeolite samples when used as received. This could be the reason of observing less adsorption capacity compared to the synthetic zeolites. Pretreatment of natural zeolites was not practiced in order to keep the operational costs down.

Looking at the images of lignite, it can be said that the demineralized samples have smaller particle sizes than raw coal samples.

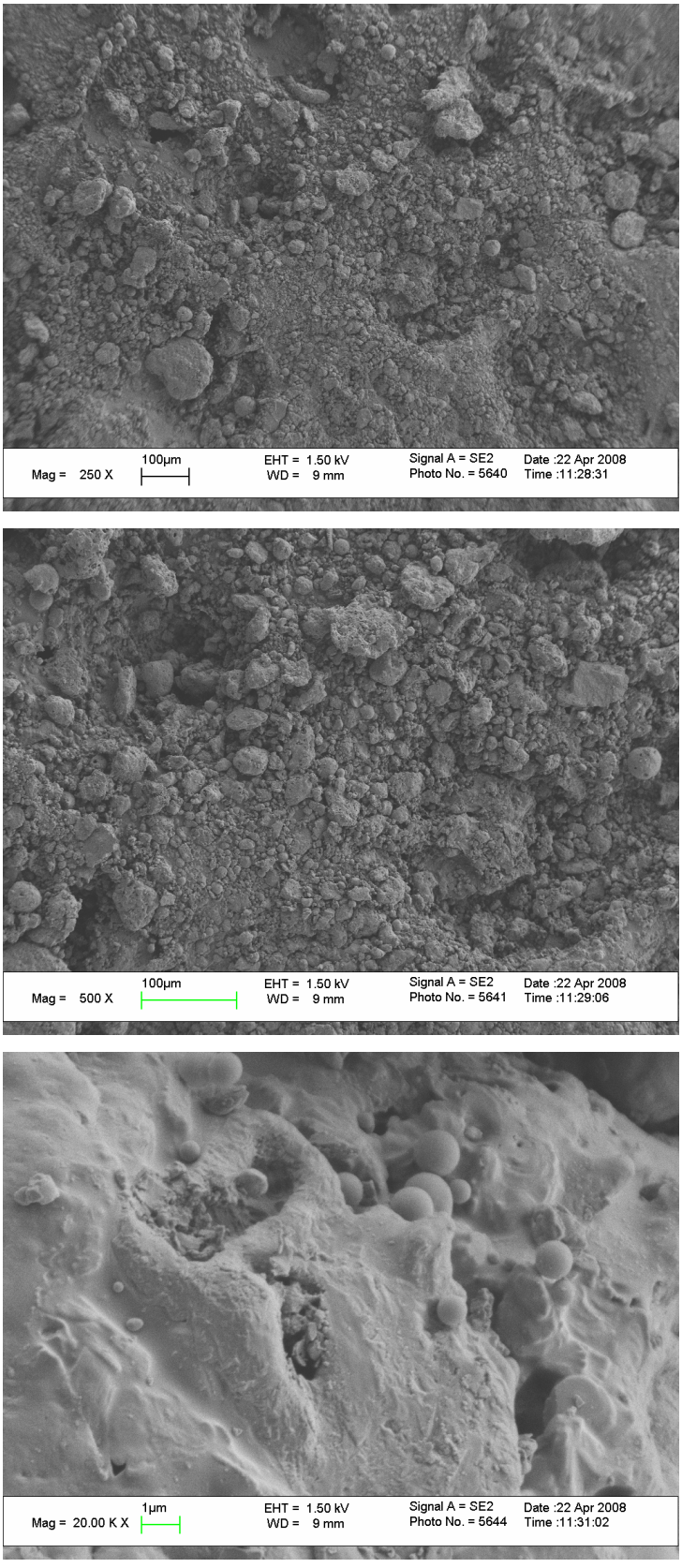



**Figure 4.5.** SEM images of fly ash

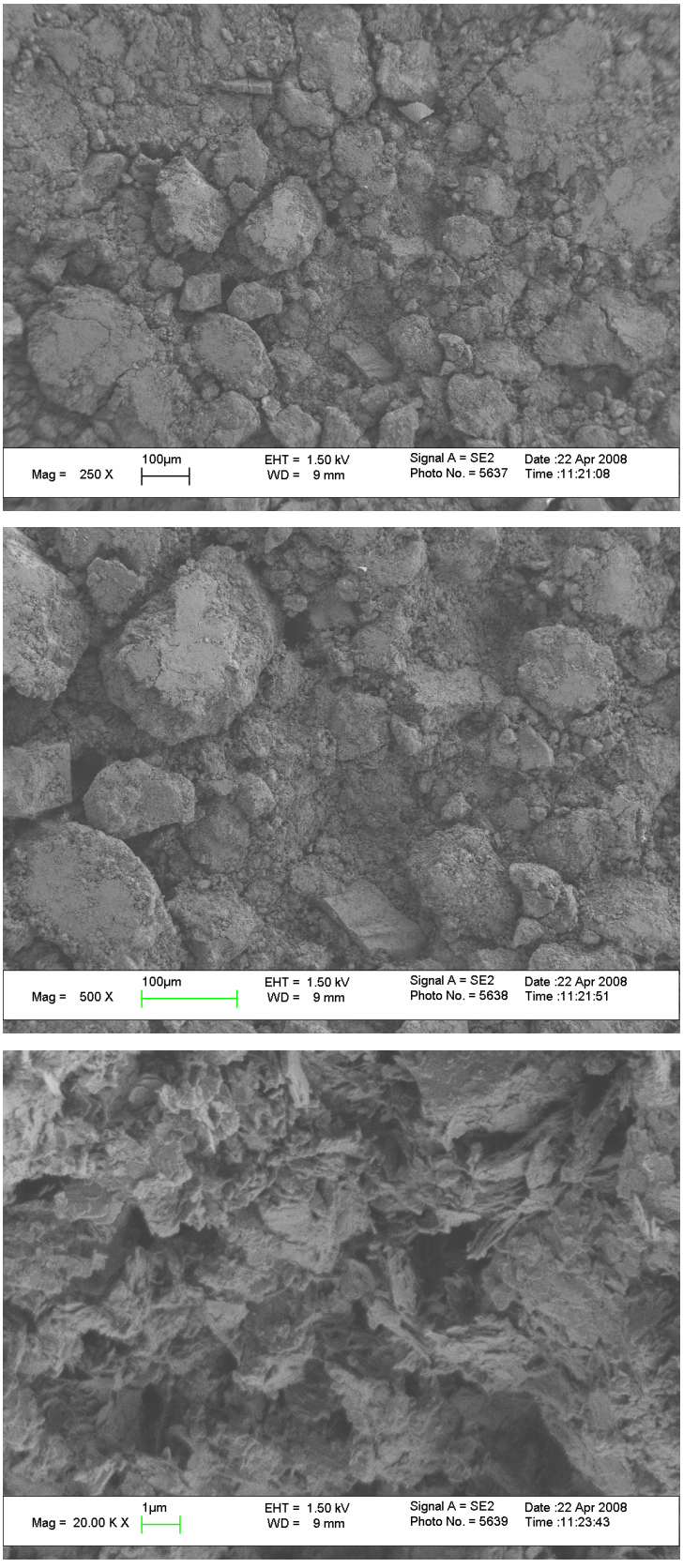
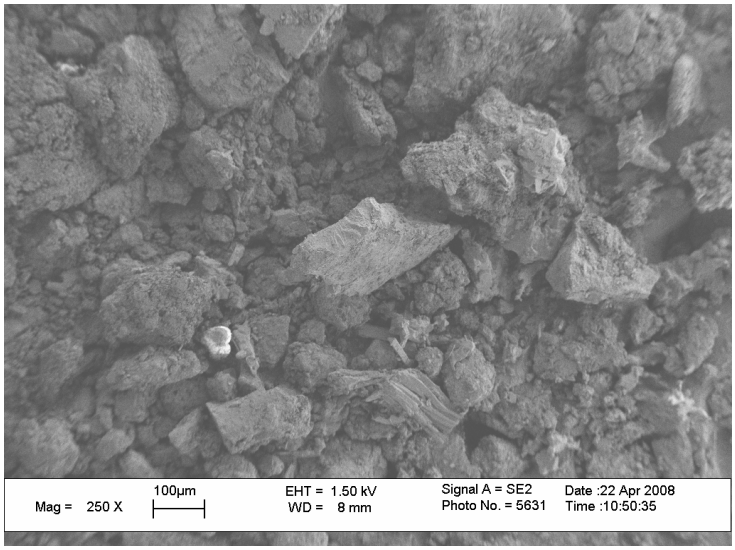
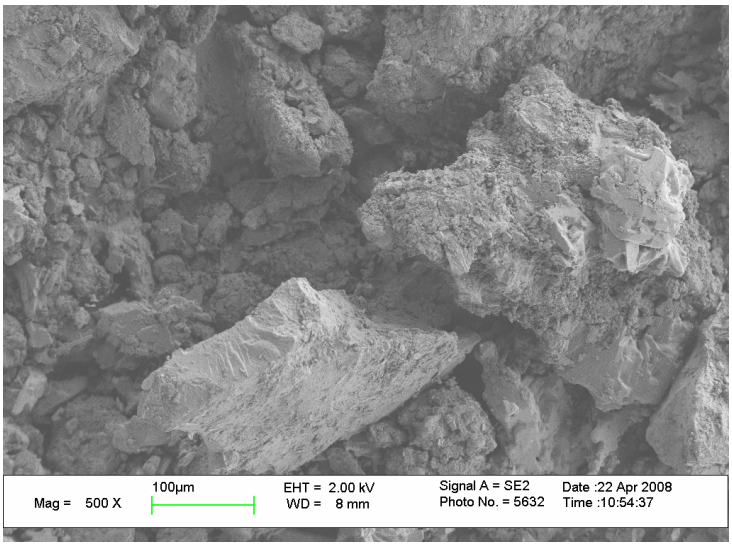



**Figure 4.6.** SEM images of clinoptilolite



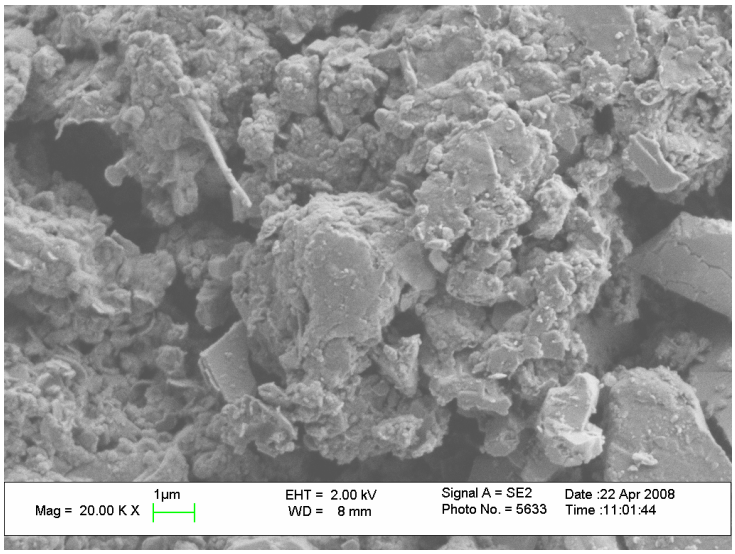




**Figure 4.7.** SEM images of lignite before demineralization

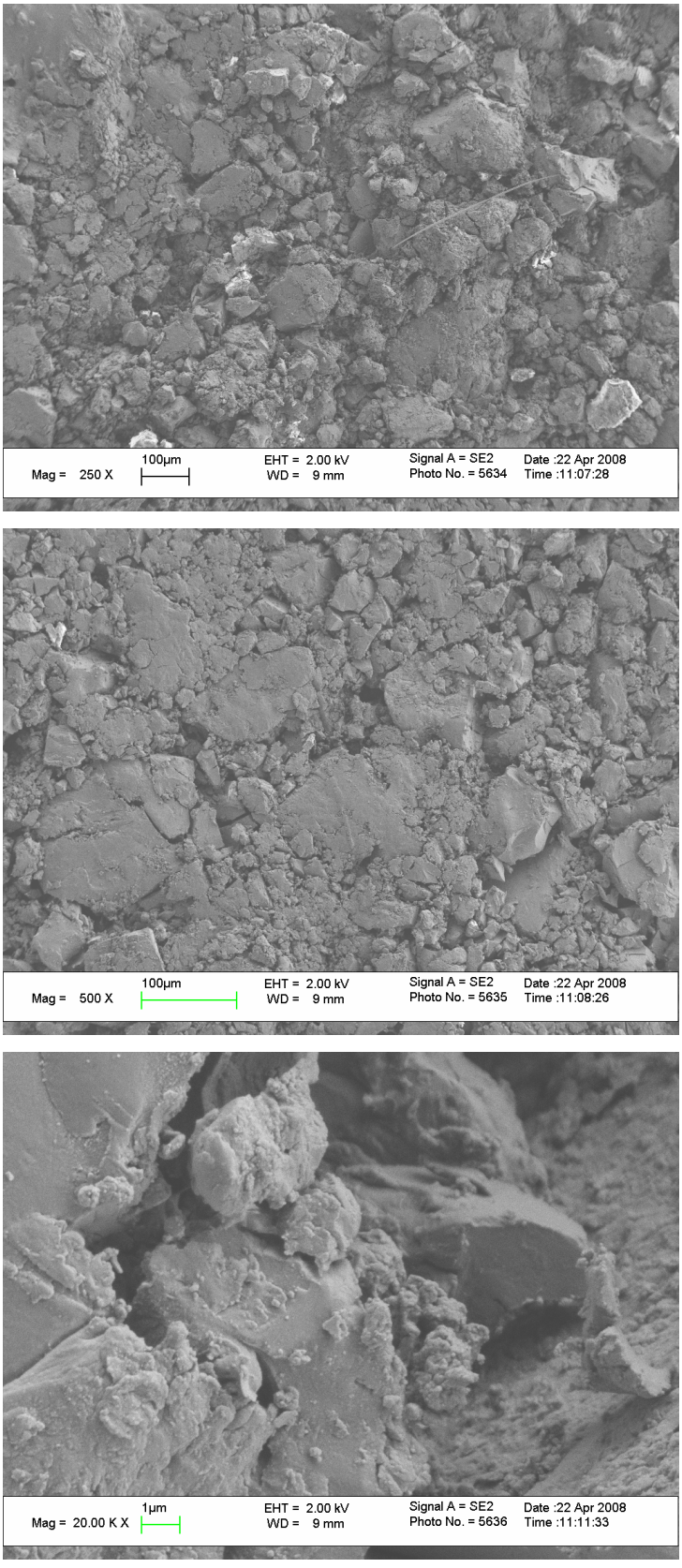



**Figure 4.8.** SEM pictures of lignite after demineralization

The surface and pore size analysis results of the adsorbents are given in table 4.2. As presented in table the surface area value of fly ash (7.24 $m^2/g$) is smaller than that of demineralized lignite (10.24 $m^2/g$) and zeolite (31.14 $m^2/g$). On the other hand, the pore radius of fly ash is enhanced (with a value of 575.03 Å) compared to demineralized lignite and zeolite (23.67 and 22.18 Å respectively). This may be an important reason of enhanced adsorption of boron on fly ash compared to other adsorbents.

**Table 4.2.** BJH surface and pore size analysis results of the adsorbents

| | **Surface Area ($m^2/g$)** | **Pore Volume (cc/g)** | **Pore Radius (Å)** |
|---|---|---|---|
| **Fly ash** | 7.24 | 0.19 | 575.03 |
| **Demineralized lignite** | 10.24 | 0.08 | 23.67 |
| **Zeolite** | 31.14 | 0.11 | 22.18 |

### 4.2. Adsorption

Batch adsorption experiments were performed for different parameters: pH, adsorption time, initial boron concentration and the amount of adsorbent. For fly ash experiments temperature was also added as a parameter.

During the experimental studies, it was observed that the raw lignite sample obtained from Kemerköy did not perform any adsorption. Moreover, the boron concentration of the aqueous solutions increased with a value of 1-2 ppm after adsorption experiments. On the other hand, demineralized lignite adsorbent adsorbed about 17 % of the boron ions of the boric acid solution (Table 4.2). The reason for this may be that the lignite samples contain boron minerals as well, which were removed during the demineralization process.

**Table 4.3.** Concentration data of the boric acid solutions without any adsorbent added and treated with carbon (coal) adsorbent (at 25 $^{o}$C, pH~10)

| Sample # | Adsorbent | Volume of solution (ml) | Amount of adsorbent (g) | Conc. of sol'n. (after ads.) (ppm) |
|---|---|---|---|---|
| **0 (blank)** | none | 50 | 0 | 17.9 |
| **1** | raw lignite | 50 | 1,05 | 19,7 |
| **2** | raw lignite | 50 | 1,12 | 19,4 |
| **3** | raw lignite | 50 | 1,37 | 19,1 |

The raw lignite sample was analyzed by ICP to determine if there is any B in its structure. The results indicate that a solution of 0,5 g of coal dissolved in 100 ml solution, which contains 1 moles of nitric acid for three moles of hydrochloric acid, includes 278 ppm of boron. Literature survey for the boron content of the seams of Beypazari lignite revealed an average value of 291 ppm also [74]. This result clarifies why there is not any adsorption observed by raw lignite adsorbent whereas an adsorption of 17 % is observed by the demineralized lignite adsorbent.

On the other hand, it is known that some minerals attached to lignite could have positive effects on adsorption. The fact that all minerals are removed during the demineralization process might be the reason of not reaching high values of adsorption with the demineralized lignite adsorbent.

### 4.2.1. Adsorption Parameters

The batch adsorption experiments were performed for different parameters such as pH, adsorption time, adsorbent amount and initial boron concentration for each adsorbent. The experiments were repeated at three different temperatures for fly ash, which was determined to be the most efficient adsorbent among those used in this study.

### a. Effect of pH on boron adsorption

The pH controls the adsorption at the water-adsorbent interfaces. The form of boron in solution depends strongly on the pH and takes the forms of $B(OH)_3$ at low pHs or $B(OH)^{4-}$ at high pHs. Hence, optimization of pH for adsorption of boron was done by studying the uptake of boron over the adsorbents (fly ash, demineralized lignite and zeolite). The pH value of the solution is an important controlling parameter in the adsorption process. Adsorption of boron as a function of pH for fly ash, demineralized lignite and zeolite at 25$^{o}$C, with an adsorbent concentration of 40 g/L and an initial boron concentration of 10 ppm and adsorption time of 24 hours is presented in Fig. 4.9. The results show that boron removal by zeolite and demineralized lignite is not affected significantly by the pH of the solution. In contrast, boron removal by fly ash is strongly dependent on the pH. It seems that maximum adsorption is achieved in the pH range of 10-11 for all of the adsorbents. Decreased adsorption values are observed at lower pH values. Therefore, all adsorption experiments were conducted at pH 10. The amount of boron removed is considerably higher in the case of fly ash. When the pH is in the range of 10-11, boron removal by fly ash, increases to about 94 %. Demineralized lignite and zeolite seems to be not very effective compared to fly ash. Boron removal by demineralized coal and zeolite reaches to maximum values of about 17-18 % at the same pH values.

Analyzing results at different pHs, it may be said that the appearance of charged $B(OH)_4^-$ ions in the solution increases the boron adsorption capacity. The reason of this may be the charge interaction between the $B(OH)_4^-$ ion and positive charged or natural surfaces of adsorbents. The strong dependence of adsorption on fly ash, on pH may be due to the charge interaction of negative charged borate ion and positive charged surface of fly ash.

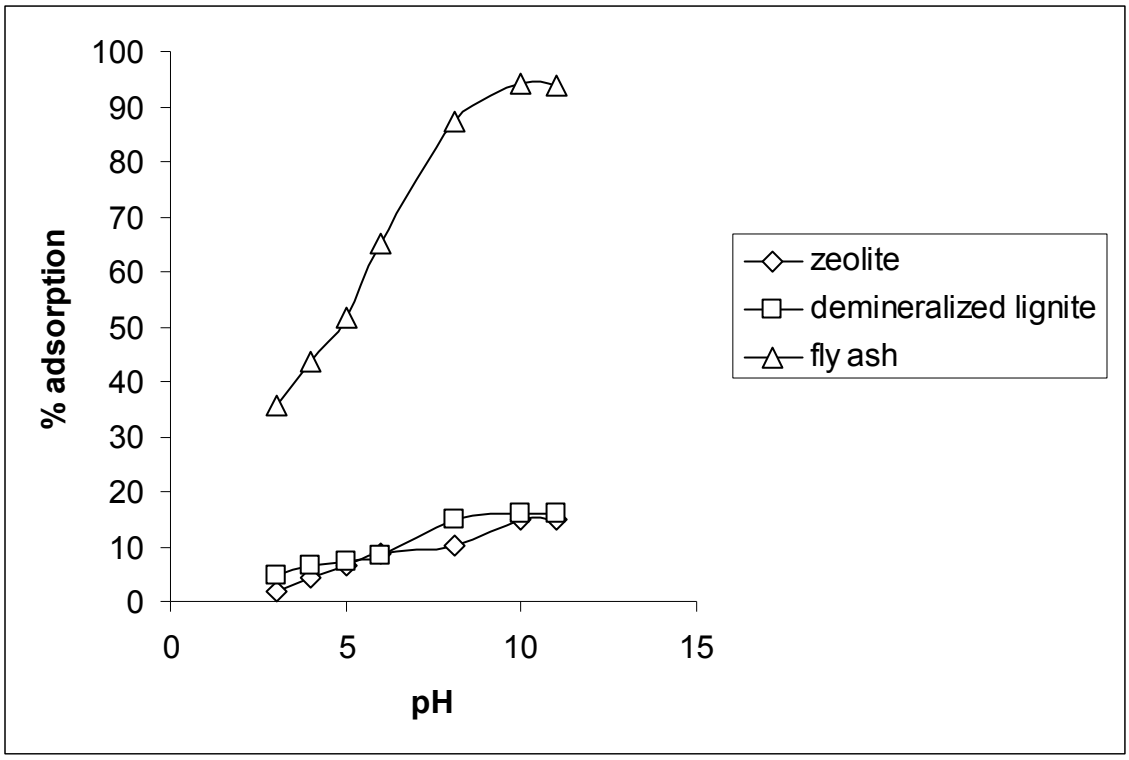



**Figure 4.9.** Percent adsorption as a function of pH for zeolite (clinoptilolite), demineralized lignite and fly ash.

### b. Effect of amount of adsorbent on boron adsorption

The amounts of adsorbent were studied and their corresponding amounts of boron removal are shown in Fig. 4.10. The amount of boron removed from aqueous boron solutions increases by increasing the adsorbent quantity for all three adsorbents. It can be observed that the process is strongly influenced in the beginning by the quantity of adsorbent that is added. A significant positive slope is revealed. The effect is more pronounced in the case of fly ash. As the amount of the fly ash is increased from 20 g/L to 100 g/L, the percentage of adsorbed boron is also increased from 47 to 95, respectively. Further increase of the amount of the fly ash does not change the percentage of the adsorbed boron. The situation in cases of demineralized lignite and zeolite is similar except that the boron adsorbed remained at a much lower value of about 17-18 % when the dose of the adsorbents was increased from 20 to 50 g/L.

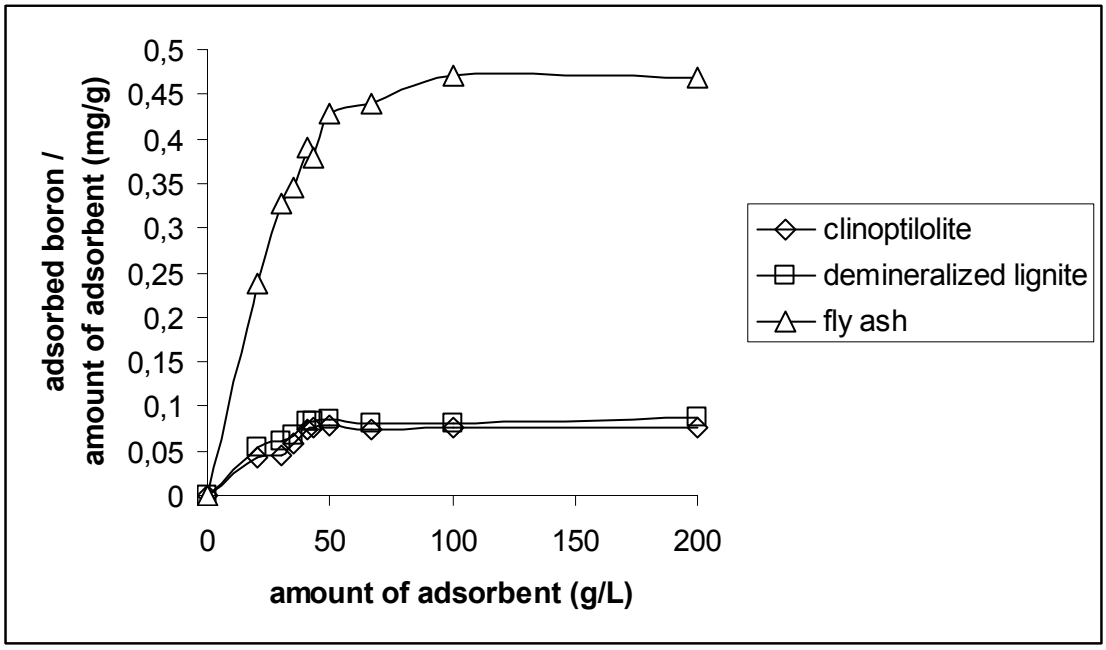



**Figure 4.10.** Adsorption amount as a function of adsorbent concentration (g/L) for zeolite (clinoptilolite), demineralized lignite and fly ash.

### c. Effect of adsorption time on boron adsorption

The effect of time, on adsorption of boron, with three different adsorbents, was studied and their corresponding amounts of boron removal, stated as a percentage, are presented in Figure 4.11. The amount of boron removed from aqueous boron solutions increases by increasing the contact time until equilibrium is reached for all three adsorbents. For zeolite and demineralized lignite, the dependence of adsorption on time is not as significant as for fly ash. For all of the adsorbents, the maximum adsorption is achieved between 20-25 hours. There is no significant decrease observed in adsorption with fly ash, demineralized lignite and zeolite, which may indicates no significant desorption occurs in about 5 hours after the system reaches equilibrium. The optimum contact time was determined to be 24 hours for all the adsorbents, and the experiments were performed for this duration for other parameters.

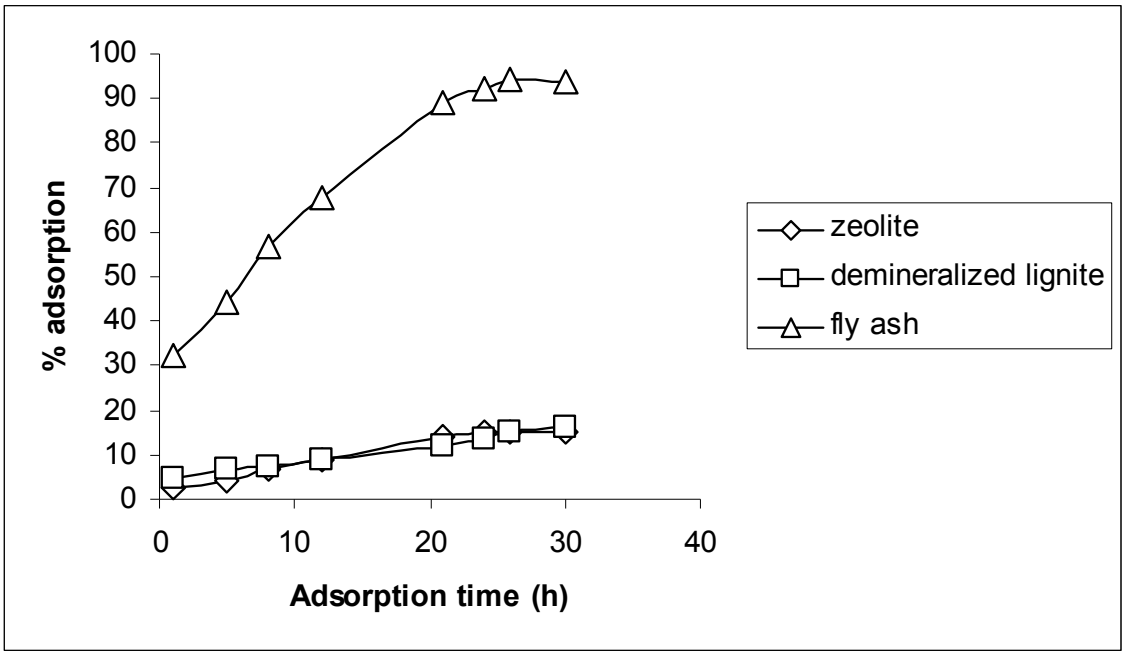



**Figure 4.11.** Percent adsorption as a function of time (h) for zeolite (clinoptilolite), demineralized lignite and fly ash.

### 4.2.2. Adsorption Isotherms

To obtain the adsorption isotherms, experiments are performed for different initial boron concentrations between 1 and 20 ppm. The experiments are performed at pH 10, for 40 g/L adsorbent amount and an adsorption time of 24 hours for each adsorbent. The Freundlich, Langmuir and Dubinin-Radushkevich (DR) isotherms are plotted for fly ash for three different temperatures (25, 35 and 45 $^{o}$C), whereas for demineralized lignite and zeolite they are plotted only for 25 $^{o}$C. The results for each adsorbent are given below, for 25 $^{o}$C. Table 4.3 shows all of the isotherm constants and $R^2$ values for each adsorbent.

The curves, of adsorbed boron on adsorbent ($C_s$, mmol/g) as a function of equilibrium boron concentration ($C_e$, mmol/L), for fly ash at different temperatures are shown in Fig. 4.12 and those of demineralized lignite and zeolite at 25 $^{o}$C are shown in Figure 4.13. As can be seen in these curves, it can be concluded that the amount of boron adsorbed increased as its equilibrium concentration in solution increased. These results indicate that the amount adsorbed increases steadily with concentration until a plateau is reached where surface of the adsorbent practically is saturated. No further adsorption occurs at this stage.

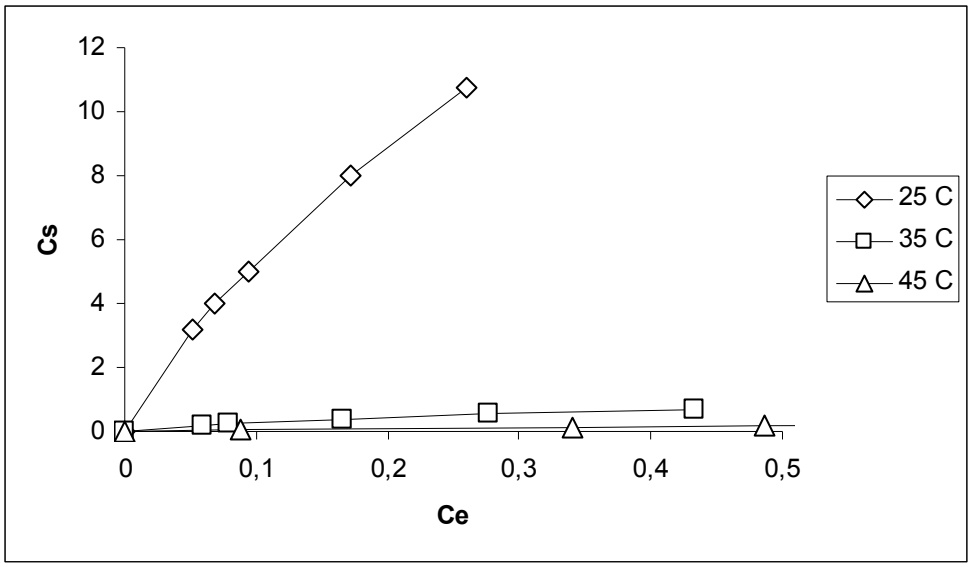



**Figure 4.12.** $C_e$ vs $C_s$ for fly ash at different temperatures

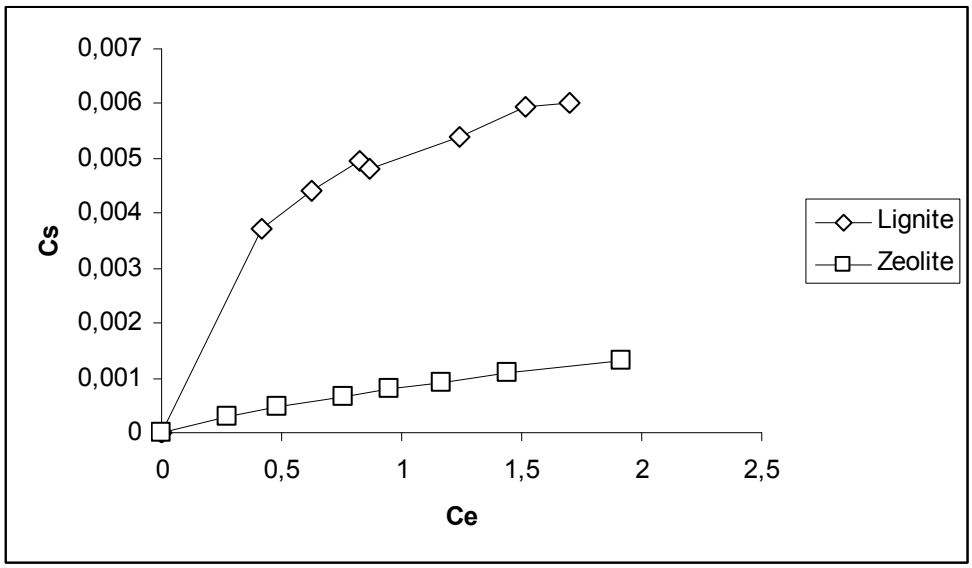



**Figure 4.13.** $C_e$ vs $C_s$ for demineralized lignite and zeolite at 25 $^{o}$C

### a. Fly Ash

Freundlich isotherm for fly ash at 25 $^{o}$C is given in Figure 4.14, whereas Langmuir and Dubinin-Radushkevich isotherms are given in Figure 4.15 and 4.16, respectively for this temperature. (The results for different temperatures are given in the Appendix section). It is observed that the adsorption data of boron on fly ash is best represented by the Freundlich isotherm, whereas Langmuir isotherm is also considerable in this case.

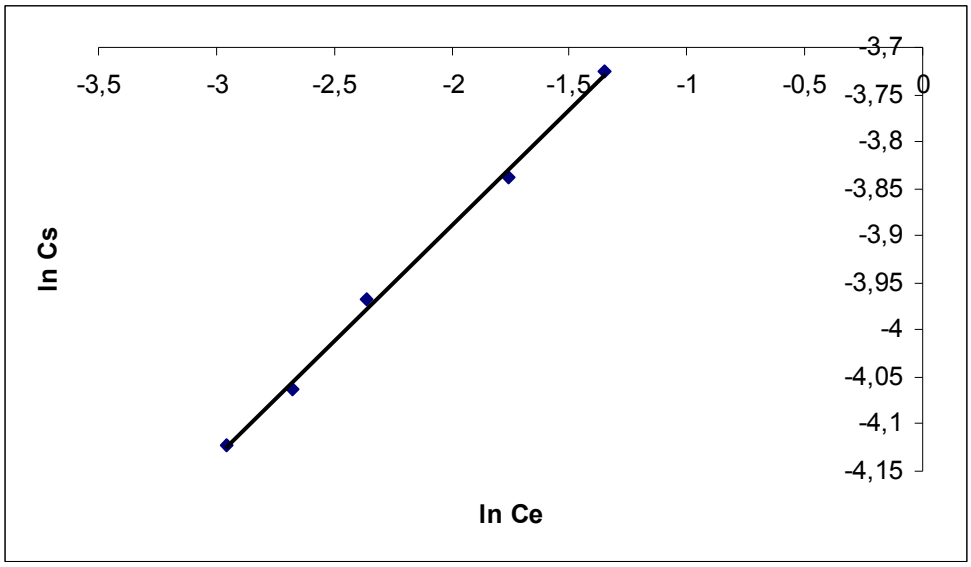



**Figure 4.14.** Freundlich isotherm for fly ash at 25 $^{o}$C

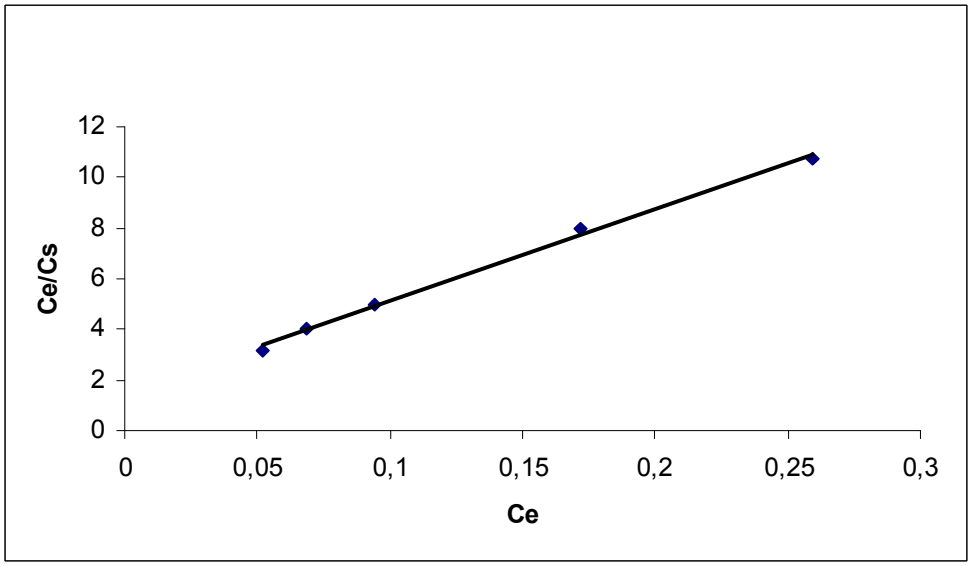



**Figure 4.15.** Langmuir isotherm for fly ash at 25 $^{o}$C

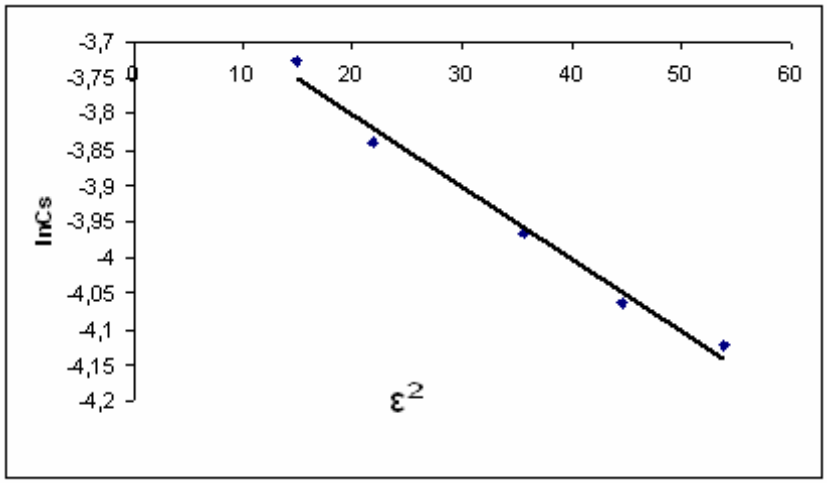



**Figure 4.16.** Dubinin-Radushkevich isotherms for fly ash at 25 $^{o}$C

### b. Demineralized Lignite

Freundlich, Langmuir and Dubinin-Radushkevich isotherms for demineralized lignite is presented in Figures 4.17, 4.18 and 4.19 respectively. Langmuir isotherm can be stated to fit the best to the adsorption data for this adsorbent.

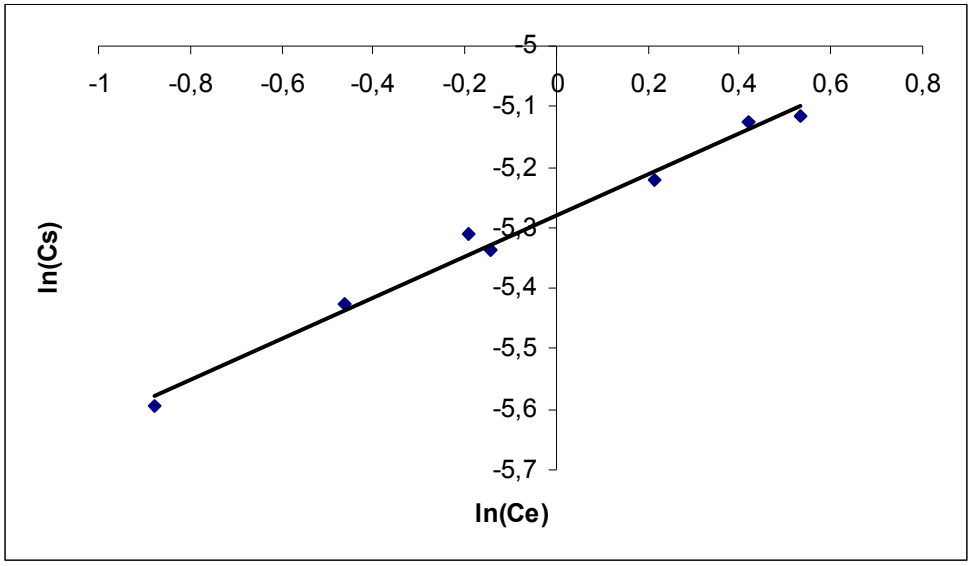



**Figure 4.17.** Freundlich isotherm for demineralized lignite at 25 $^{o}$C

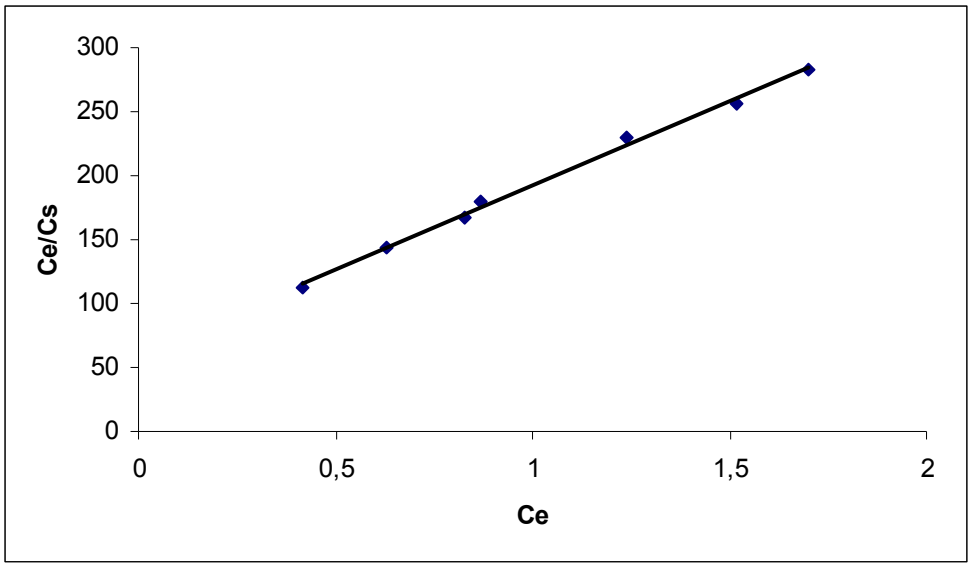



**Figure 4.18.** Langmuir isotherm for demineralized lignite at 25 $^{o}$C

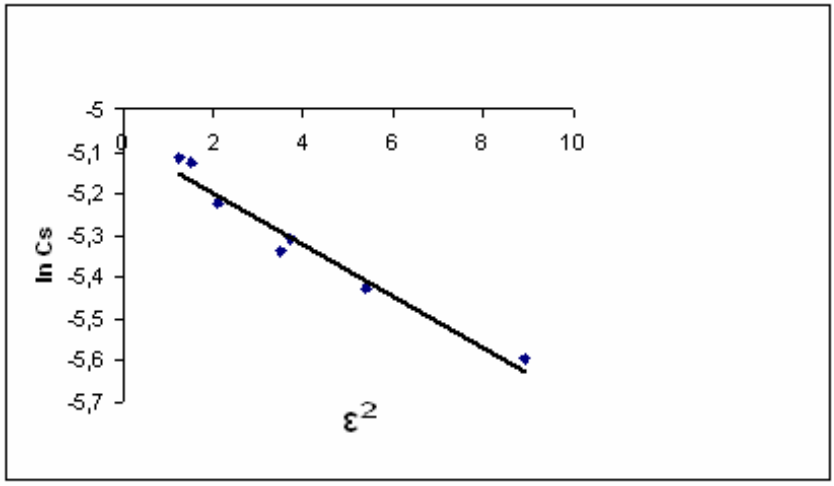



**Figure 4.19.** Dubinin-Radushkevich isotherm for demineralized lignite at 25 $^{o}$C

### c. Zeolite

Figures 4.20 - 4.22 present the Freundlich, Langmuir and Dubinin-Radushkevich isotherms for zeolite. As in the fly ash adsorbent case, Freundlich isotherm is the most suitable one for adsorption of boron on zeolite.

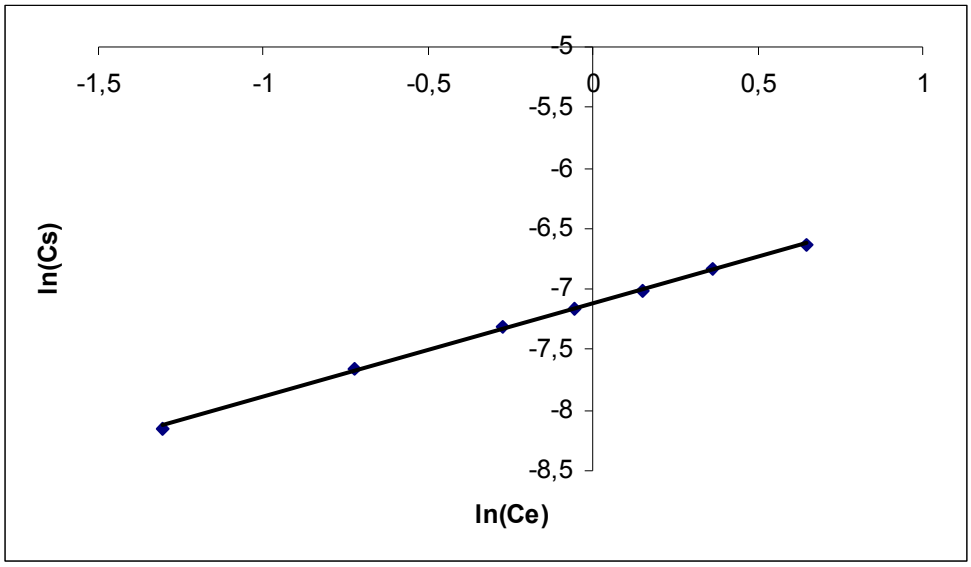



**Figure 4.20.** Freundlich isotherm for zeolite at 25 $^{o}$C

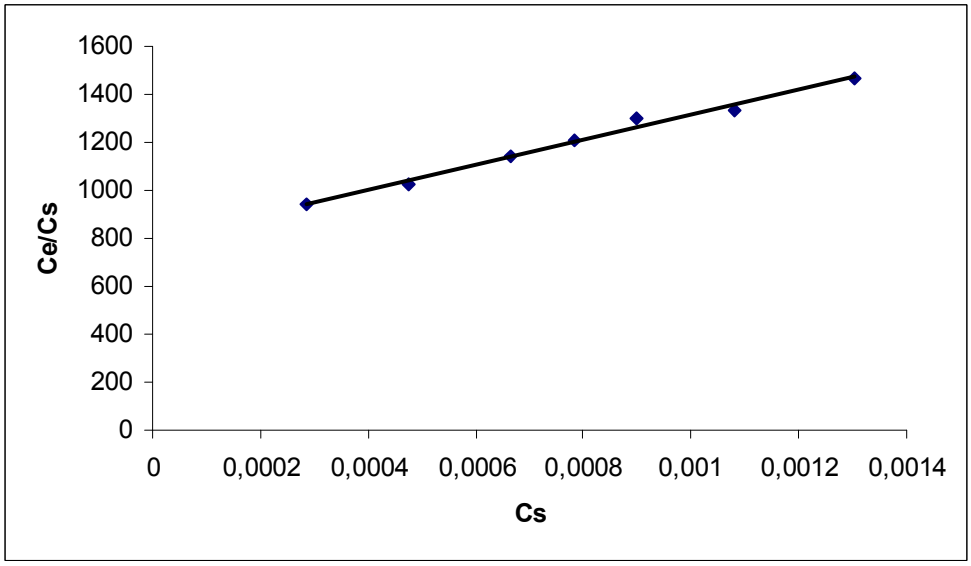



**Figure 4.21.** Langmuir isotherm for zeolite at 25 $^{o}$C

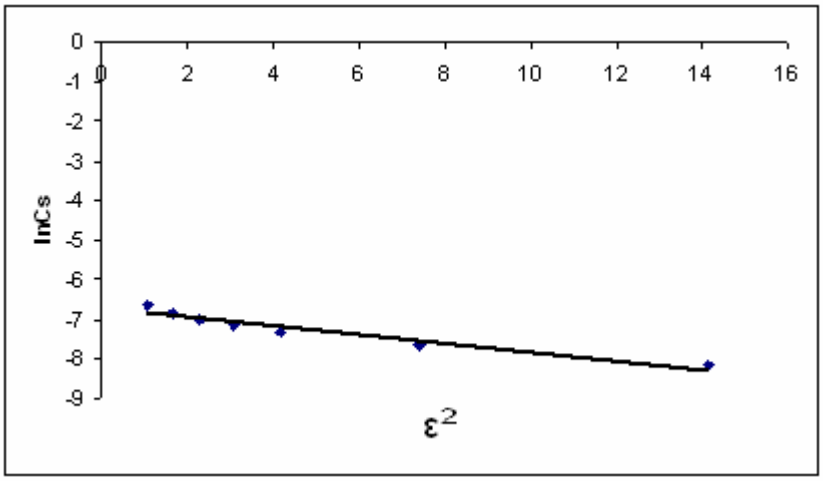



**Figure 4.22.** Dubinin-Radushkevich isotherm for zeolite at 25 $^{o}$C

### d. Isotherm Constants

The isotherm constants for all three adsorbents at 25 $^{o}$C, is presented in Table 4.3**.** The isotherm that fits the best is determined for each adsorbent by looking at the $R^2$ values that indicate the closeness of the plot to a linear plot ($R^2$ values closest to one, indicates the best match to a linear plot). The adsorption characteristics of demineralized lignite fit best to Langmuir isotherm with an $R^2$ value of 0.9953. For zeolite and fly ash adsorbents, Freundlich isotherms fit better than other isotherms with $R^2$ values of 0.9985 and 0.9973 respectively. On the other hand, because the $R^2$ value for Freundlich isotherm of fly ash is not significantly less than that, Langmuir model is also considerable for demineralized lignite.

**Table 4.4.** Langmuir, Freundlich and Dubinin-Radushkevich isotherm constants for different sorbents at 25 $^{o}$C.

| | **Langmuir Constants** | | | **Freundlich Constants** | | | **Dubinin-Radushkevich Constants** | | |
|---|---|---|---|---|---|---|---|---|---|
| **Sorbent** | $R^2$ | $C_m$, mmol/g | $L$ | $R^2$ | $K_f$, mmol/g | $n_f$ | $R^2$ | $X_m$, mol/g | $k$, mol$^2$/kJ$^2$ |
| Demineralized lignite | 0.9953 | 0.0076 | 2.172 | 0.9868 | 0.0051 | 0.3380 | 0.9593 | 0.0063 | 0.0622 |
| Zeolite | 0.9792 | 0.0031 | 0.365 | 0.9985 | 0.0008 | 0.7711 | 0.9380 | 0.0012 | 0.1082 |
| Fly ash | 0.9969 | 0.0275 | 24.52 | 0.9973 | 0.0334 | 0.2452 | 0.9852 | 0.0273 | 0.0101 |

Values in Table 4.3 reveal the extent of adsorption on different adsorbents. $C_m$ and $L$ explaines why the adsorption on fly ash was much greater compared with those of demineralized lignite and zeolite. $L$ is the equilibrium constant relating rates of adsorption and desorption ($L=k_a/k_d$). Greater values of L indicate higher rates of adsorption rather than desorption, which means more material adsorbed on the adsorbent. $L$ value for the fly ash is much greater than those of other adsorbents and that was also an indication why the extent of adsorption on fly ash was the greatest among other adsorbents.

As implied by the values of $n_f$, sorption seems to be highly nonlinear for fly ash and demineralized lignite but close to unity in the case of zeolite. This indicates a fast decrease in the fixation capacity of the adsorbent sites as the initial concentration is increased. Since Freundlich isotherm does not predict a maximum coverage for a given adsorbent, it is hard to say that $K_f$ corresponds to the maximum sorption capacity. The value of $K_f$ can, however, be correlated with the adsorption capacity of the adsorbent under the particular experimental conditions and can be useful in providing a qualitative comparison for the fixation ability of a given adsorbent towards different adsorbates.

As mentioned in the second chapter, the DR isotherm is the one which gives information about the mechanism of the adsorption. The mean free energy (E) of adsorption is the free energy change when one mol adsorbate is transferred from infinity in solution to the surface of the adsorbent. The DR constants as well as the E values are presented for fly ash at three different temperatures (Table 4.4). E values are in the range of (3.11–7.03) kJ/mol. Since E values are less than 8 kJ/mol, the type of adsorption is a physical adsorption due to weak van der Waals forces [29, 30]. $X_m$ values increases with increasing temperature from 25 to 35 °C, whereas a decrease in $X_m$ values is observed with increasing temperature from 35 to 45 °C. The value of k increases with increasing temperature.

**Table 4.5.** Dubinin-Radushkevich constants and adsorption energies for fly ash at different temperatures.

| T, $^oC$ | $R^2$ | $X_m$, mol/g | $k$, $mol^2/kJ^2$ | -E, kJ/mol |
|---|---|---|---|---|
| 25 | 0.9852 | 0.0273 | 0.0101 | 7.036 |
| 35 | 0.9838 | 0.8699 | 0.0297 | 4.103 |
| 45 | 0.9514 | 0.2758 | 0.0515 | 3.116 |

### 4.2.3. Thermodynamic Studies

In order to understand the effect of temperature on the adsorption process, thermodynamic parameters should be determined at various temperatures. A plot of $\ln K_c$ against 1/T renders a straight line, as shown in Figure 4.23.

The thermodynamic parameters of the adsorption of boron on fly ash are presented in Table 4.5. As can be seen from Table 4.5, $K_c$ values are increasing with the increase in temperature. In contrast, $\Delta G^0$ values decreased when the temperature increased.

**Table 4.6.** Equilibrium constants and standard Gibb's free energy changes for fly ash at three different temparatures

| T ($^o$C) | $K_c$ | $\Delta G^o$ (kj/mol) |
|---|---|---|
| 25 | 0.1961 | 4.2683 |
| 35 | 0.2437 | 3.6918 |
| 45 | 0.2768 | 3.4939 |

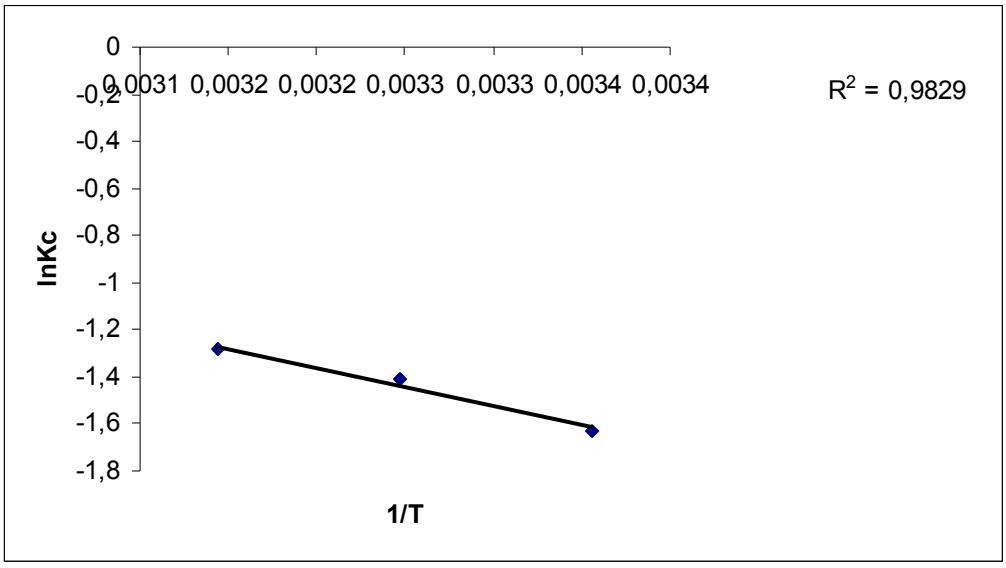



**Figure 4.23.** 1/T versus $\ln K_c$

The $\Delta S^o$ and $\Delta H^o$ values of the adsorption of boron on fly ash adsorbent were found as 0.0322 kJ/molK and 13.6134 kJ/mol, respectively. A positive value of $\Delta S^o$ indicates the increased randomness at the solid/solution interface during the adsorption of boron on all of the fly ash samples and the increased freedom of the molecules of the system. The reason of this may be the increase in free water molecules in the system. There is both borate-water interaction and surface-water interaction in the system before adsorption. During the adsorption, the borate ions interacts with the surface of adsorbents, so water molecules are released from the surface and free water amount increases in the system. Positive values of $\Delta H^o$ show the endothermic nature of the process. $\Delta G^o$ values decrease when the temperature increases. The positive values of $\Delta G^o$ imply that the adsorption of boron on fly ash samples is not spontaneous. In addition to this, since positive values of $\Delta G^o$ decrease with an increase in temperature, the nonspontaneous nature of adsorption is inversely proportional to the temperature.

### 4.2.4. Kinetic Studies

The effect of contact time on the amount of boron adsorbed onto fly ash samples was examined at the optimum initial concentration of boron. As presented before, the maximum amounts of adsorption of boron onto fly ash samples were observed at about 24 hours. This can be accepted as the optimum contact time. Several kinetic models have been applied with an attempt to find the adsorption mechanism of boron onto fly ash samples. The pseudo-first order equation, the pseudo-second order equation, and the intraparticle diffusion model were employed with the equations presented in Chapter 2.

The kinetic parameters for adsorption of boron on fly ash for each model is presented in Table 4.6. The parameters are determined using following estimations:

#### a. Pseudo First Order Kinetic Model

For pseudo first order model, 1/t versus $1/q_t$ was plotted to investigate the fit of pseudo-first-order-kinetics to boron adsorption (Figure 4.24). From the linear correlation analysis it is observed that the value of the correlation coefficient ($R^2$) is 0.86.

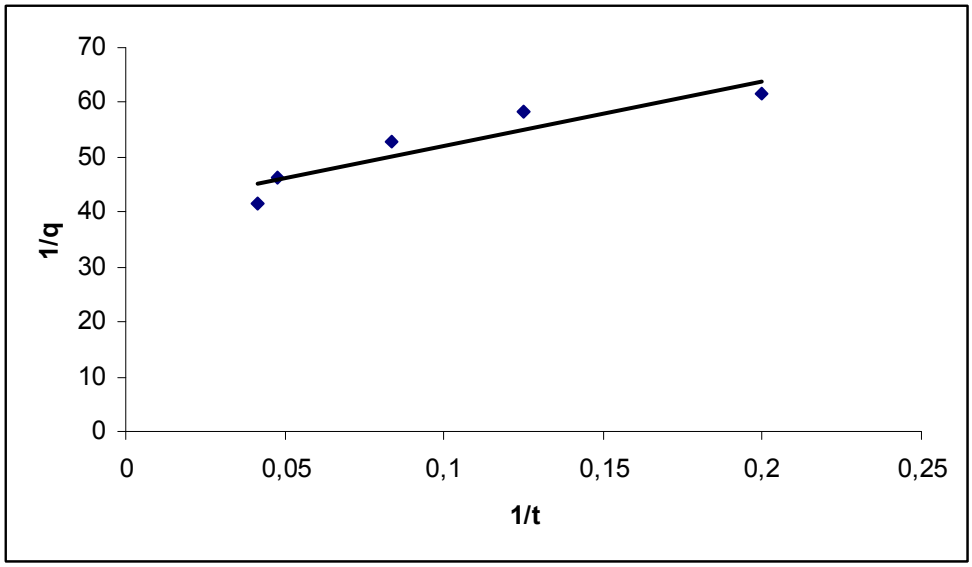



**Figure 4.24.** Pseudo first order kinetic plot for the adsorption of boron on fly ash

### b. Pseudo Second Order Kinetic Model

Figure 4.25 was obtained by plotting t versus $t/q_t$ to analyse the pseudo second order model. As shown in figure, the linearity of the plot implies the applicability of the pseudo-second-order kinetic equation for adsorption of boron onto fly ash, with an $R^2$ value of 0.9828.

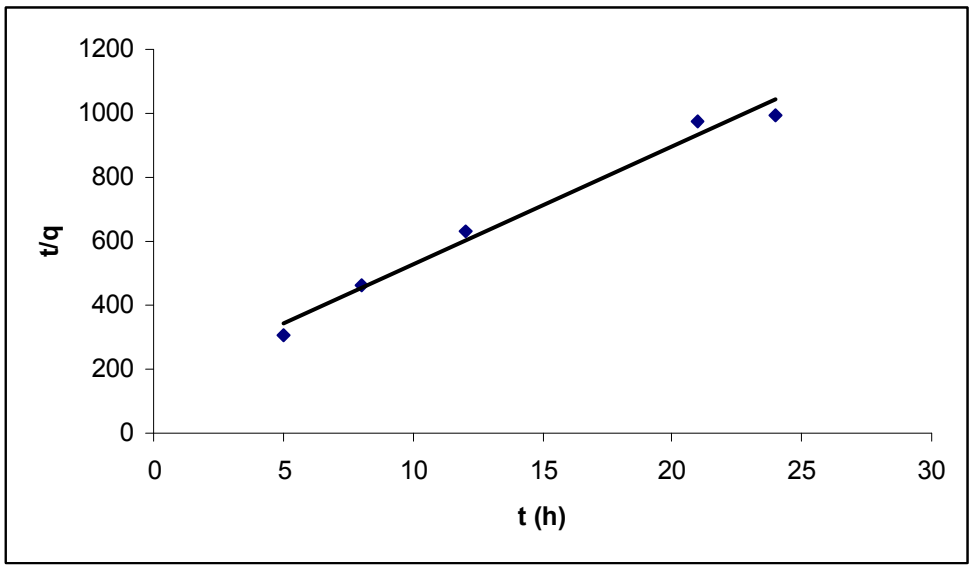



**Figure 4.25.** Pseudo second order kinetic plot for the adsorption of boron on fly ash

### c. Intraparticle Diffusion Model:

For the third model, the plot of $t^{1/2}$ versus qt was tested. Correlation coefficient for intraparticle diffusion value was found as 0.9583.

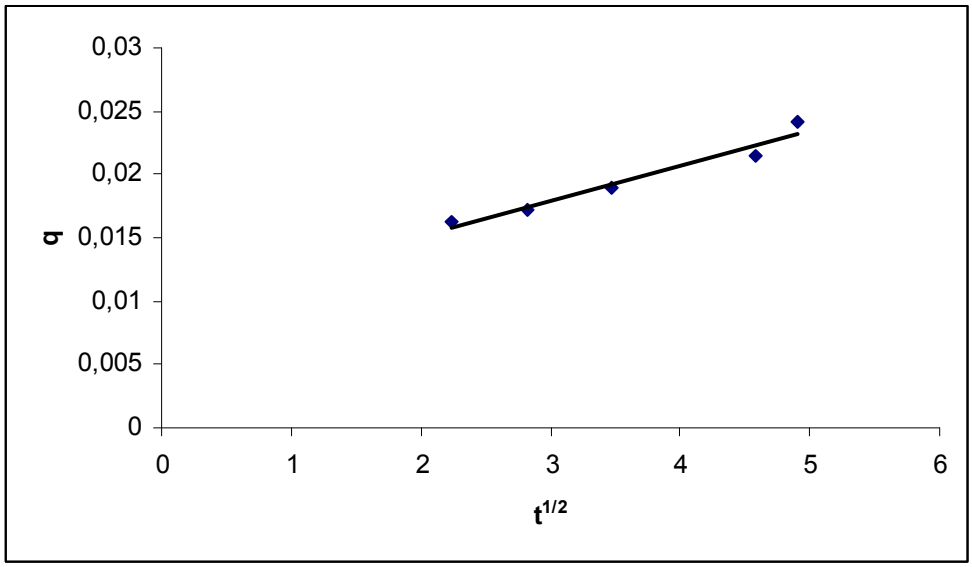



**Figure 4.26.** Intraparticle model for the adsorption of boron on fly ash

Applying all three models to kinetics data, the pseudo-second order model was determined as the most suitable model for adsorption of boron on fly ash. Since intraparticle diffusion model coefficient ($R_p^2$) was also relatively significant, it might also be concluded that intraparticle diffusion of the boron species had also some effect in the adsorption kinetics.

Kinetic parameters for adsorption of boron on fly ash, for all three models, are presented in Table 4.6.

**Table 4.7.** Kinetic Parameters for adsorption of boron on fly ash

| Adsorbent | $k_1$ ($h^{-1}$) | $q_1$ (mg/g) | $R_1^2$ | $k_2$ (g/mgh) | $q_2$ (mg/g) | $R_2^2$ | $k_p$ ($mg/gh^{1/2}$) | C (mg/g) | $R_p^2$ |
|---|---|---|---|---|---|---|---|---|---|
| Fly ash | 2.922 | 0.0025 | 0.8685 | 8.5158 | 0.0271 | 0.9828 | 0.0028 | 0.0095 | 0.9583 |

The rate constant of pseudo-second-order adsorption of boron on fly ash was found as 8.516 g/mg-h. The maximum adsorption capacity was found as 0.027 mg/g for pseudo-second-order model.

# CHAPTER 5

# CONCLUSIONS

In conclusion, this study is about removal of boron ions from boron containing aqueous solutions using lignite, natural zeolite (clinoptilolite) and fly ash as adsorbents. This study demonstrated that boron removal was controlled by the material type and several parameters such as pH, amount of adsorbent and adsorption time. The experiments show that more than 90 percent of boron can be removed from boric acid solution due to interaction with fly ash under suitable conditions (at pH 10 and a temperature of 25 $^{o}$C, with 40 g/L adsorbent, for an adsorption time of 24 hours). Utilization of zeolite and demineralized coal were not as successful in removing boron from aqueous solutions. Percentage of boron removed by zeolite and demineralized coal remained at about 17-18 % under the same conditions for these adsorbents.

The characterization of adsorbents were done using SEM, XRD and BET methods. The surface areas of fly ash, demineralized lignite and zeolite are obtained as 7.24, 10.24 and 31.14 $m^2/g$ respectively, whereas their pore radius values were 575.03, 23.67 and 22.18 Å respectively.

Using the adsorption data for different initial boron concentrations, adsorption isotherms were obtained. Adsorption characteristics of boron on zeolite is determined to fit to Freundlich isotherm the best, whereas the adsorption on demineralized lignite can be explained by Langmuir isotherm. For fly ash, the adsorption can be considered to fit both Langmuir and Freundlich isotherms.

Dubinin-Radushkevich isotherms were used to calculate adsorption energies and to analyze adsorption of boron on fly ash thermodynamically and kinetically. The mechanism of adsorption is determined as physical adsorption due to weak van der Waals forces, since E values are less than 8 kJ/mol. $\Delta G^{o}$ of adsorption of boron on fly ash was found between 3 and

4.5 kJ /mol for different temperatures. The $\Delta S^o$ and $\Delta H^o$ values of the adsorption were found as 0.0322 kJ/molK and 13.6134 kJ/mol, respectively. To analyze the adsorption kinetically, three models were considered: pseudo-first-order, pseudo-second-order and intraparticle diffusion model. The pseudo-second-order model was determined to be the most suitable for adsorption on fly ash, whereas the effect of intraparticle diffusion is also considered to be significant.

# CHAPTER 6

# RECOMMENDATIONS

Future work in this area may be related to investigating alternate natural adsorbents for adsorption of boron from waters. One approach may be screening other types of fly ash samples. It is recommended that the surface area and pore size are determined prior to the adsorption experiments.

Another approach could be treating the natural zeolites before the adsorption experiments. In this work, the natural zeolite is used on an "as received" basis in order to keep the processing costs down. If the natural zeolite sample is washed with dilute hydrofluoric acid, some of the silica can be washed away, and silica/ alumina ratio can be decreased, making the zeolite more hydrophilic. Washing followed by treating the zeolite is above 250 $^{o}$C could result in an increase its surface area and adsorption capacity.

This work consisted of batch experiments. If large quantities of water needs to be treated, continuous, or cyclic adsorption processes in fixed bed adsorbers becomes necessary. So future experiments may be done in a continuous fashion where natural adsorbents are used in a fixed bed column.

Experiments may be repeated with real waste water obtained from industrial sites. This will show the effect of competitive adsorption with other ions in the waste water on adsorption capacity of boron.

Finally, desorption characteristics of boron adsorbed on fly ash can be studied. This will assess the suitability of boron containing fly ash as an agricultural nutrient for boron deficient soils.

## CHAPTER 7

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# APPENDIX

## A.1. Characterization

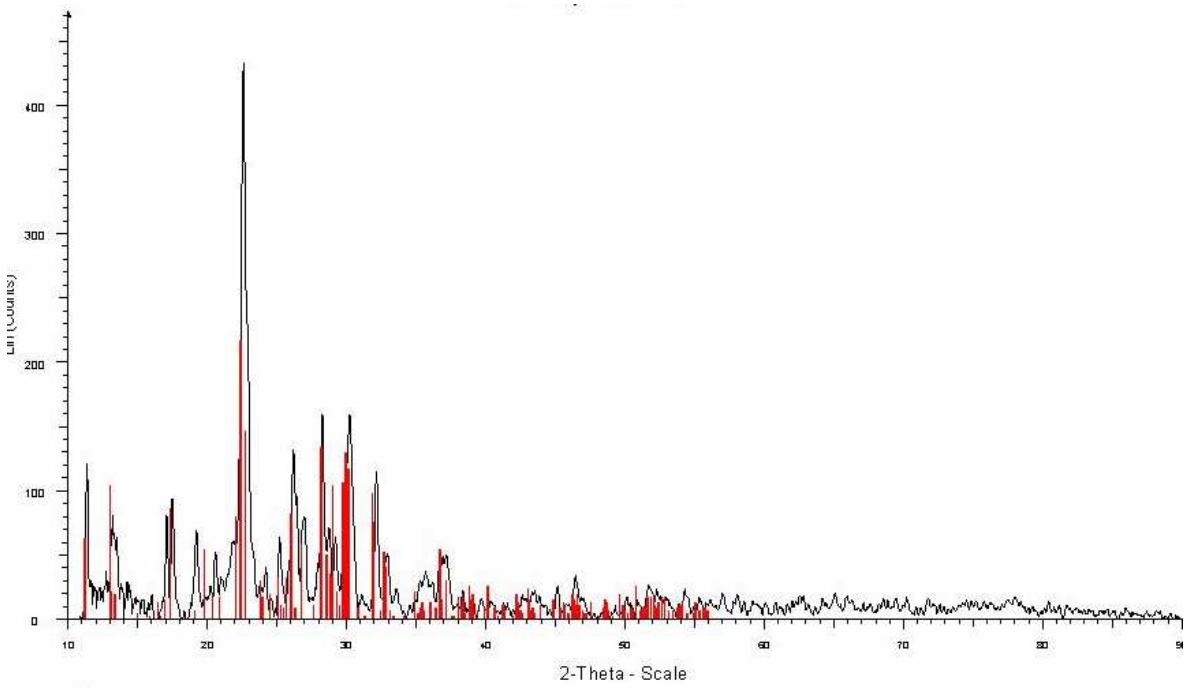


**Figure A.1.** Theoretical XRD peaks of clinoptilolite

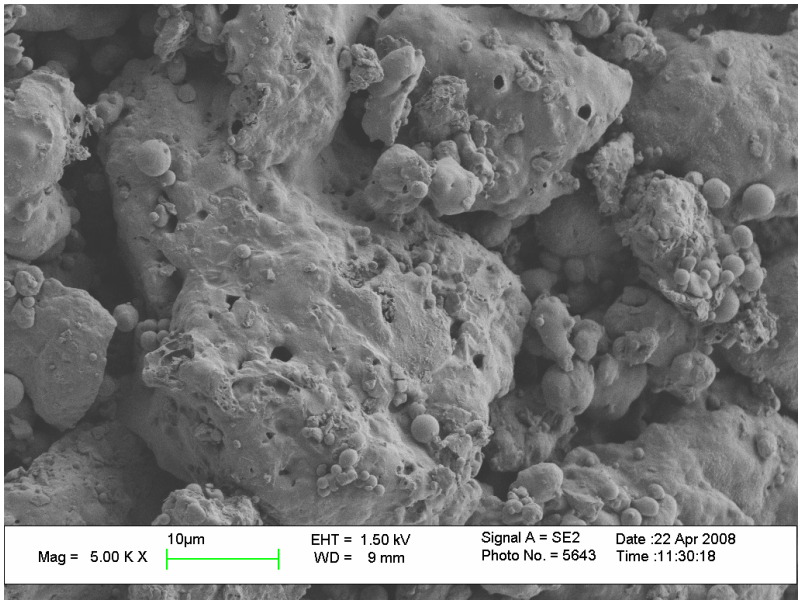


**Figure A.2.**SEM image of fly ash at 5 KX magnitude

## A.2. Adsorption Isotherms

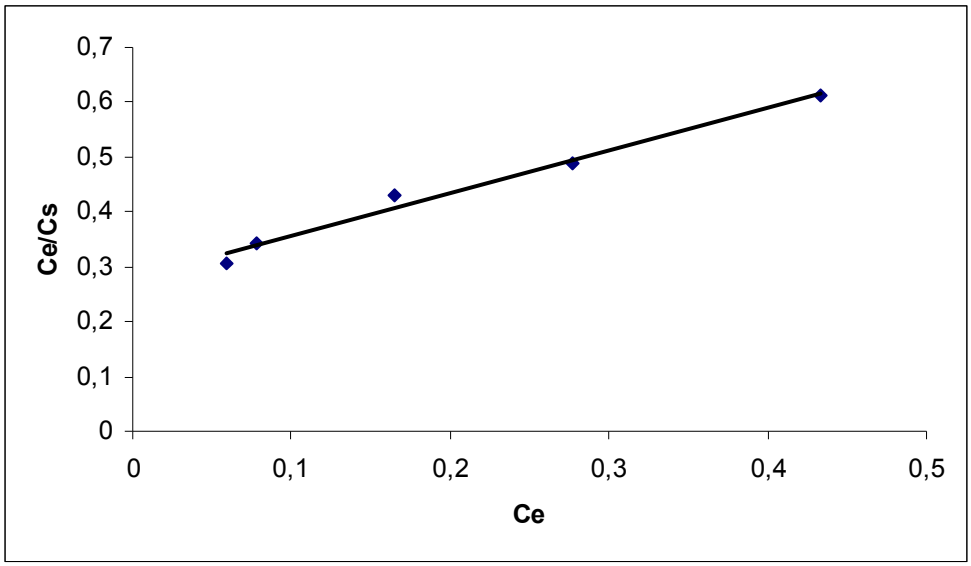


**Figure A.3.** Langmuir isotherm for fly ash at 35 $^{o}$C

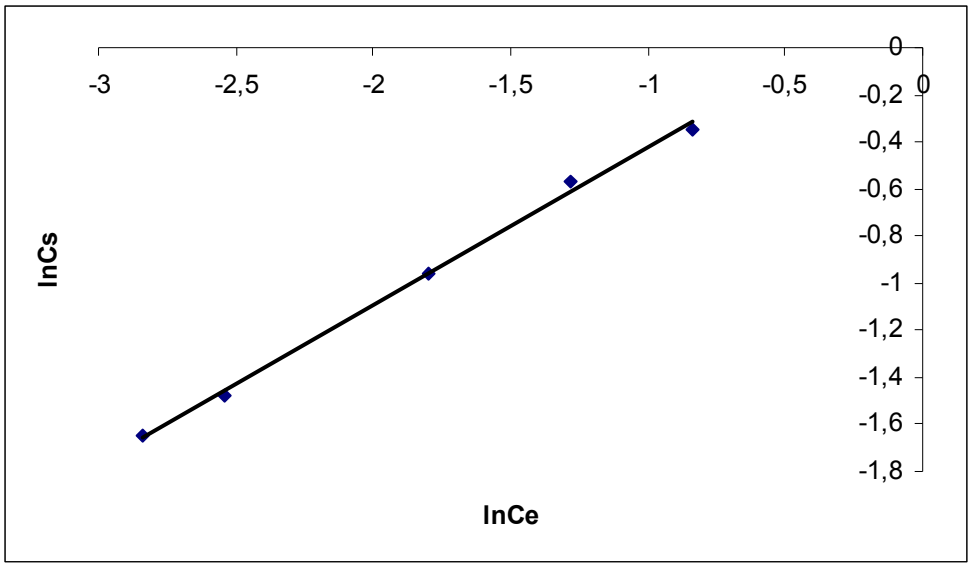


**Figure A.4.** Freundlich isotherm for fly ash at 35 $^{o}$C

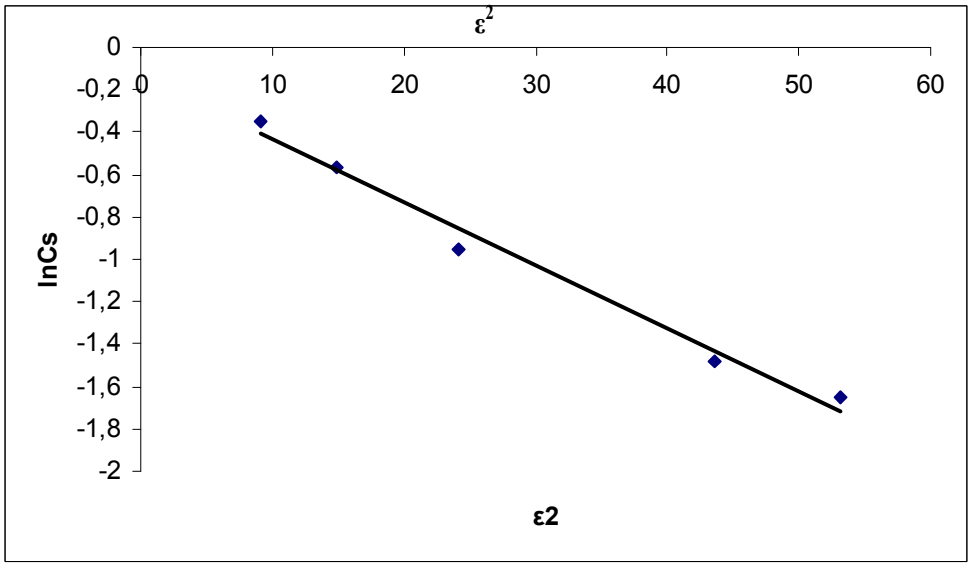


**Figure A.5.** Dubinin-Radushkevich isotherm for fly ash at 35 $^{o}$C

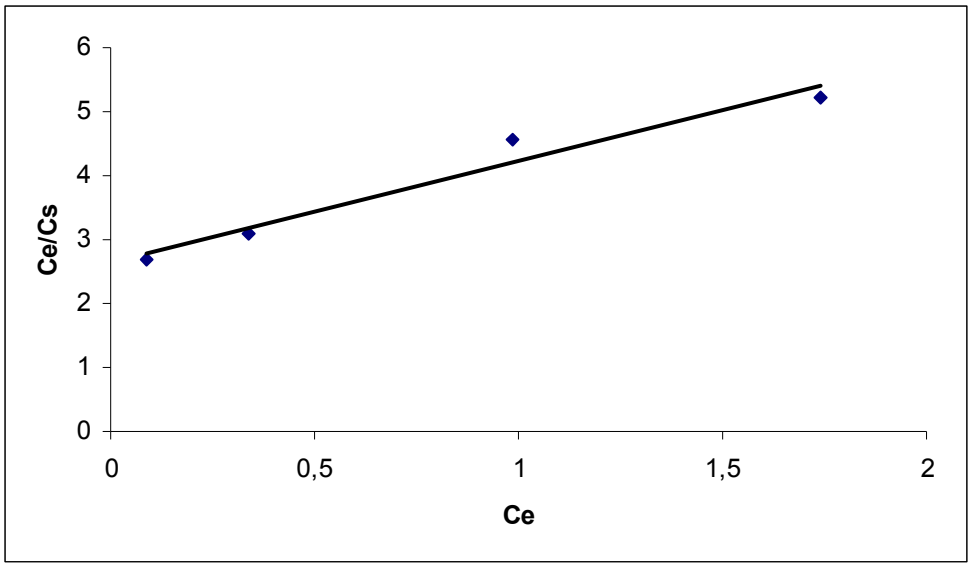


**Figure A.6.** Langmuir isotherm for fly ash at 45 $^{o}$C

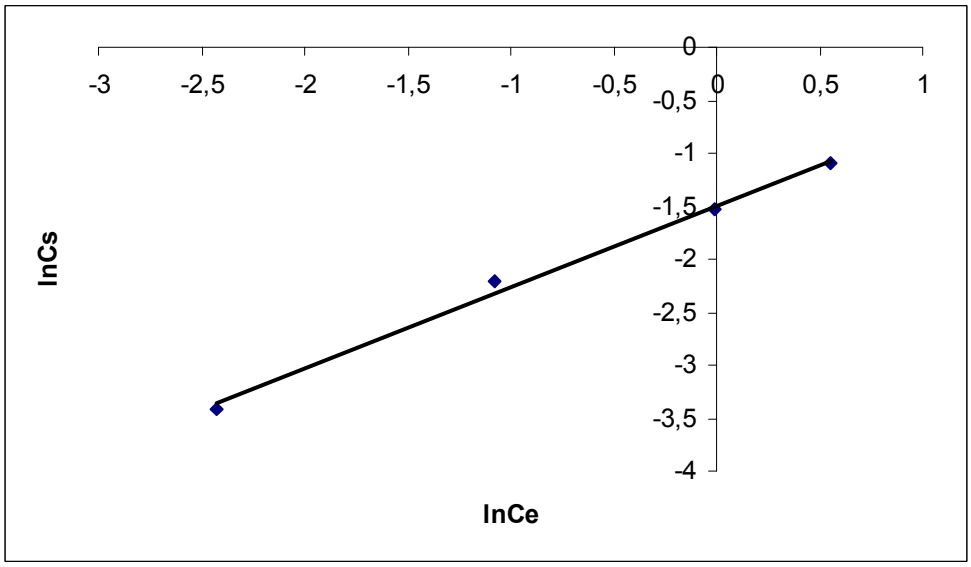


**Figure A.7.** Freundlich isotherm for fly ash at 45 $^{o}$C

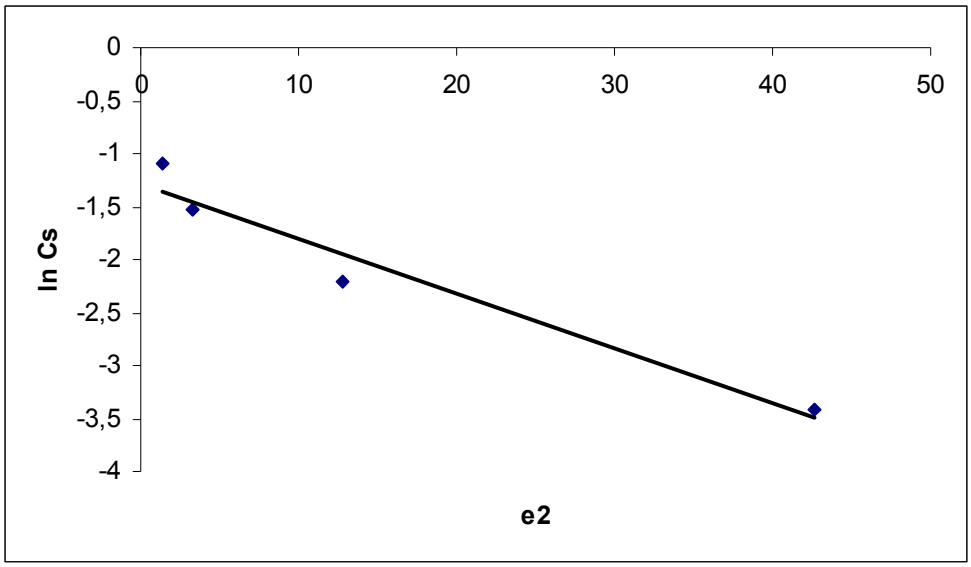


**Figure A.8.** Dubinin-Radushkevich isotherm for fly ash at 45 $^{o}$C

## A.3. Boron and Boric acid

### A.3.1. Boron

The primary source of both boron and borates is the mining of boron-containing minerals. Some examples of these minerals are: colemanite, ulexite, tincal, and kernite. The certain deposits that can be mined economically are located in arid regions of Turkey, USA, Argentina, Chile, Russia, China, and Peru. The total world production of boron minerals was approximately 2,750,000 tones in 1994 and about 250 000 tones of boron, corresponding to 800,000 tones of boron oxide ($B_2O_3$), was present in commercial borate products manufactured from these minerals [69].

The commercial borate compounds that are used in the manufacture of many different commercial products include insulation and textile-grade fiberglass, borosilicate glass, fire retardants, enamels, ceramic glazes, frits, laundry bleach (sodium perborate), agricultural fertilizers and herbicides as well as many other applications.

Boron enters the environment mainly through natural processes and from human activities. Mainly, the natural sources which causes to boron releases are: boron-containing rocks, seawater, volcanic activity and other geothermal releases such as geothermal steam and hot water. The human activities, which mainly release boron through are: agricultural use; burning of domestic waste, crop residues and wood fuel; power generation using fossil fuels such as coal and oil; waste from borate mining and processing; the use of borates and perborates in the home and industry; leaching from treated wood or paper; and disposal of sewage and sewage sludge.

Boron can be released to fresh water such as rivers and also to the water contained within soils. This occurs through weathering processes and, to a much smaller extent, through human discharges such as sewage and treated effluent releases to rivers.

Boron is present in the environment in boron-containing compounds called borates. Borates dissolved in water can adsorb onto, and desorb from, the many different surfaces found in rivers and streams. The amount of borate adsorption depends on the water's pH and the concentration of borate in the water. Borates dissolved in water are very stable, and do not react with oxygen or other chemicals which may be present in the water, or undergo changes from one type of borate to another. Also, animals and plants are not able to convert borates from one form to another by biological processes. Boron is also adsorbed onto soil particles. The type of soil is important for the degree of adsorption and to what extent the adsorption is reversible or irreversible (whether boron can be removed again by water running through the soil or not). The soil characteristics are also important for the amount and type of boron binding to soil. These characteristics are pH of the soil, the amount of salt, organic matter, iron, aluminum oxides, hydroxy-oxides and clay present in the soil.

Considering the amount of boron, in soils, the average boron concentration is approximately 30 mg/kg of soil (ranging from 10 mg/kg of soil up to 300 mg/kg of soil). The boron concentration depends on the type of soil, the amount of organic matter, which contains boron, and the amount of rainfall, which can remove boron from the soil. In surface water, concentrations of boron depend on the amount of boron present in the soils and rocks of the drainage area, and on the proximity of the drainage area to the ocean. The ocean provides boron both by the deposition of vaporized boric acid on the drainage area, and by infiltration of boron-containing seawater in tidal regions and estuaries. Surface waters can also receive boron inputs from effluent discharges, both from industrial processes and from municipal sewage treatment. Concentrations of boron in surface water range widely, from 0.001 mg/L to as much as 360 mg/L. However, average boron concentrations are typically well below 0.6 mg/L.

In ambient air, boron concentrations range from 0.5 to approximately 80 ng/$m^3$ of air, with an average for air laying over continental land masses of 20 ng/$m^3$ of air.

**TableA.1.** Regions of the world and representative boron concentrations in surface water [69]

| **Regions of the world** | **Representative boron concentrations in surface water** |
|---|---|
| Europe, Pakistan, Russia, and Turkey | Mean concentrations below 0.6 mg/L |
| Japan, South Africa, and South America | Generally below 0.3 mg/L |
| North America | Typical concentrations below 0.1 mg/L (with only 10% above 0.4 mg/L) |

Boron accumulates in aquatic and terrestrial plants but does not increase in concentration through the food-chain. Concentrations of boron in plants depend on their environment. In marine invertebrate animals and fish, boron concentrations are similar to the boron levels found in the oceans. Two freshwater fish species have been found to take up very little boron, as the concentrations in their bodies only reached 30% of the level found in the water in which they live.

Humans are exposed to boron through diet, from drinking water, and from some consumer products including soaps and detergents, body building supplements, bottled water, fertilizers, pesticides, preservatives, and cosmetic, oral hygiene, eye care, and deodorant products. They may also, to a much smaller extent, ingest boron from the soil or breathe it in with the air. Within the diet, the richest sources of boron are fruits, vegetables, legumes, and nuts. Dairy products, fish, meats and most grains contain very little boron. People who work in borax mines and refining plants, or in industries which use borates to manufacture other products, may be exposed to boron during their work. Inhalation of dusts which contain boron is the most significant route of exposure at work for workers in these industries. Dermal absorption of boron may also occur if damaged skin is in contact with boron compounds.

There are known effects of boron on humans and mammals. Once ingested, borates are almost completely absorbed in the gut and appear rapidly in the blood and body tissues. In mammals, boron is distributed evenly throughout the body fluids. Unlike soft tissues and blood, bone takes up boron selectively to give levels more than four times higher than in blood serum. Boron also remains longer in bone, before elimination. Boric acid is not metabolized (transformed) within the body. Thus the types and relative amounts of boron-containing compounds in the body will be the same in all mammals. Boron is eliminated by the same route and at the same speed in humans and rats, with more than 90% of boron being eliminated through the urine and with half of the boron being eliminated in 24 hours or less.

Rats are the main species used in laboratory studies to determine the no-observed-adverse-effect level (NOAEL) of a substance. These similarities in the way boron acts in humans and rats increase the reliability of predicting effects in humans from effects in rats.

In laboratory animals, boron mainly affects the reproductive system and the development of the fetus. In rats, the NOAEL for boron intake is 9.6 mg/kg body weight per day. The first effect which becomes apparent at greater intake level is reduced fetal body weight. At a boron intake level of about 13 mg/kg maternal body weight per day, the weight of rat fetuses is slightly reduced, and rib anomalies may be present. At approximately 55 mg/kg body weight per day rats experience changes in the testicles and become sterile. In the rabbit, malformations of the heart and the circulatory system can be seen at boron intake levels of

approximately 25 mg/kg body weight per day. In the mouse, fetal body weight can be affected at approximately 80 mg/kg body weight per day [69].

Because of the lack of human data and the limited amount of animal data, the EPA (U.S. Environmental Protection Agency) has classified boron as "not classifiable as to human carcinogenicity" in 1994. Only a few studies on humans have investigated health effects associated with exposure to boron compounds. These show that exposure can be associated with short-term and reversible irritant effects on the upper respiratory tract, nasopharynx, and eyes. The sole long-term study did not identify any long-term health effects. Two studies on people exposed to boron found no effects on human fertility and no statistically significant change in the relative number of boys and girls born. No studies have yet investigated other reproductive outcomes, such as time-to pregnancy, conception delays, spontaneous abortions, and sperm quality. In order to identify populations which might be sensitive to boron exposure, and to evaluate reproductive effects more fully, further study of the role of other lifestyle or behavioral factors in relation to health and fertility is needed.
The effect of boron has been determined for several types of organisms in the environment, but more information is available for some types of organism than for others. Some of the information covers the effects of short-term exposure to boron, while other information focuses on long-term or chronic exposure. The information may be available for several types of organism within a group or it may be available for only one type. The amounts and types of information available for different species are important in the overall judgment of the relative sensitivity of environmental organisms to boron in the environment.

The data of done researches show that bacteria are much less sensitive to boron, compared to other chemicals. Protozoa are somewhat more sensitive. Algae, for which boron is an essential nutrient, also have low sensitivity to boron. Invertebrates also have low boron sensitivity, as determined from many long-term studies. Fish are the most sensitive species to boron. The experts assembled by the World Health Organization (WHO) to write the IPCS (International Program on Chemical Safety) document decided, based on the sensitivity of the various tests and the numbers of tests for the different types of organisms, that a boron level of 1 mg/L water would cause no adverse effect on the environment.

Boron is an essential micronutrient for plants, but different plant species require different boron levels for optimum growth. Several roles that boron plays within the plant cell are in cell division, in the metabolism, and in the cell membrane.

In plants, there is only a narrow margin between boron deficiency and excess boron uptake leading to toxicity. Boron deficiencies in terrestrial plants have been reported in many countries. Boron deficiency occurs when boron leaches out of the soil, particularly in humid regions with light-textured, acid soils. Boron excesses usually occur in soil solution, i.e. the water found in the soil containing soluble material, from geologically young deposits, arid soils and soils derived from marine sediments. It also occurs in soils contaminated by human activities, such as releases from coal-fired power plants and mining operations. Irrigation water containing boron is one of the main sources of high boron levels leading to toxicity on agricultural land.

### A.3.2. Boric acid

Boric acid is a water soluble, very weak monobasic acid with a pKa of 9.2 [69]. It has a trigonal geometry as shown in Figure 7.1.

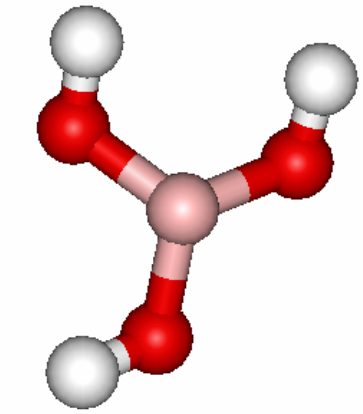

**Figure A.9.** Boric acid structure. Pink sphere represents B atom, red ones are O atoms and gray ones are H.

When dissolved in water, boric acid acts as a Lewis acid by accepting a hydroxyl ion to form the borate anion:

$H_3BO_3 + H_2O \leftrightarrow B(OH)_4^- + H^+$

The borate anion has a tetrahedral geometry (Figure 7.2).

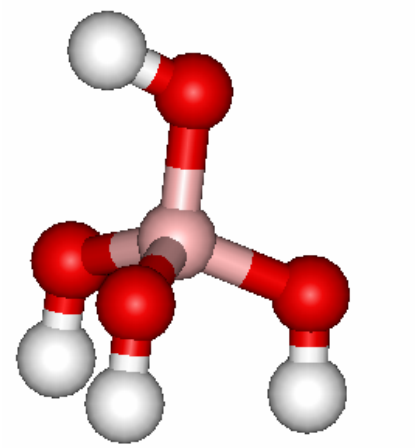

**Figure A.10** Borate anion structure. Pink sphere represents B atom, red ones are O atoms and white ones are H.

Ligand exchange is a mechanism whereby anions become specifically adsorbed onto mineral surfaces forming inner-sphere surface complexes [69]. Ligand exchange with surface hydroxyl groups can be started as the mechanism of B adsorption on aluminum oxide minerals [70- 72]. Inner-sphere complexes contain no water molecules between the adsorbing anion and the surface functional group; while outer-sphere complexes contain at least one water molecule between the adsorbing anion and the surface functional group [73].

### 7.3.5. Boron - Measurement Methods

In order to measure the amount of boron present in water, soil, or in biota such as plants or other environmental species, the boron is usually removed from the sample by a process called extraction. Hot water is used to extract boron from soil. Acid and chloroform are used to extract boron from water, while acid can be used to extract boron from biological samples. Error can be introduced into the measurement process if extraction is not complete. The solution containing the extracted boron is then analyzed, to determine the amount of boron

originally present in the sample. For the low levels of boron present in environmental samples, sensitive measurement techniques are needed. The best techniques use ICP, or Inductively Coupled Plasma, methods, with either Atomic emission spectroscopy (AES) or Mass spectrometry (MS) used to detect the boron. ICP-MS is the most sensitive one. In addition, it requires only a small volume of sample for the measurement.