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Removal of Boron and Boron Compounds from Wastewaters

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Abstract

Boron is an essential micronutrient for plants and animals. However, it is harmful and poisonous in high doses. This study aimed to conduct studies to remove boron from the wastewater of Eti Mine Works using natural and modified adsorbents such as waste clays, zeolites, walnut shells, waste corn cobs and waste sunflowers. Firstly, adsorption studies were carried out with the wastewater taken from Emet boron operations directorate with waste clays obtained from Emet, Bandırma, Kırka, Bigadiç operations directorates and zeolite obtained from site of the Bigadiç operations directorate in a batch system of shaking, thermostat water bath. Adsorption studies were carried out using different amount of adsorbent, pH and particle size to determine the effects of these parameters on adsorption. The adsorption processes were found to be insufficient to remove boron from wastewater with high boron content as 5883 ppm using natural adsorbents. Therefore, it was decided to apply first chemical precipitation and then adsorption by using natural adsorbents. Secondly, it was aimed to eliminate high boron content in Espey Spring Water with high boron content in the Espey open pit site to improve the quality of irrigation water within the framework of social responsibility. Espey Spring Water's initial boron value was 3810 ppm. After two-stage pre-treatment with lime, its boron value was 297 ppm (92% removal efficiency). Then, the adsorption studies were carried out at the same conditions as in the first part of this study using HCl modified almond shells as adsorbent. The optimum parameters reached were as 8 g of adsorbent, at pH 10, at 150 rpm mixing speed, at 25 ºC and at 4 hours contact time. The adsorption process consisting all these optimum parameters; 66.7% removal efficiency was reached. Almond shells were found to be effective adsorbents for boron removal from springs waters, having high boron content in the scope of social responsibility considering environment and living health. These results were found to be important from an economic perspective because of evaluating natural wastes, as almond shells, in the adsorption process for boron removal.

Cite

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1. INTRODUCTION

1.1. General Information About Boron

Boron, located in III A group of periodic tables and shown as B, has semi-metallic and semi-conducting properties having atomic number as 5 and atomic weight as 10.81. It has two separate stable isotopes called B10 and B11 in nature. The most important feature that makes boron mineral important is that of being very hard and resistant to high temperatures (Baran, 2014).

In nature, boron is never found free (Baran, 2014). It tends to bond with oxygen. It is found as minerals bound to sodium, calcium and magnesium oxides and containing crystal water. These minerals are called boron salts

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(Doğan et al., 2005). The general name of boron-oxygen compounds is borate. In this way, many boron compounds are used in different branches of industry.

Industrially important boron compounds are borax (tincal, sodium-based boron compounds), colemanite (calcium-based boron compounds) and ulexite (sodium-calcium-based boron compounds). In Turkey, sodium based tincal, calcium based colemanite and sodium+calcium based ulexite are commonly found boron minerals (Ateş, 2018).

Boron is used in many areas of life; it is widely used in glass, ceramics, agriculture, cleaning-detergent, wood protection, health and flame retardant. It is also included in armor materials through the use of boron carbide in the defence industry.

1.2. Boron Chemistry

When borates are dissolved in water, other polymeric species are present in the environment along with boric acid. For example, the following species are found in the solution of borax (sodium borate) in water (Uslu, 2010).

$$Na_2B_4O_7.10H_2O \longrightarrow 2Na^+ + 2B(OH)_4^- + 2H_3BO_3 + 3H_2O \quad (1)$$

Boric acid and borates' solubility increases with temperature in water.

pH is an important parameter effecting the behaviour of water-soluble boron. Boron is present in water in the form of boric acid when the pH is less than 7 and in the form of borate at the pH values greater than 10.5. This situation can be seen in Figure 1.

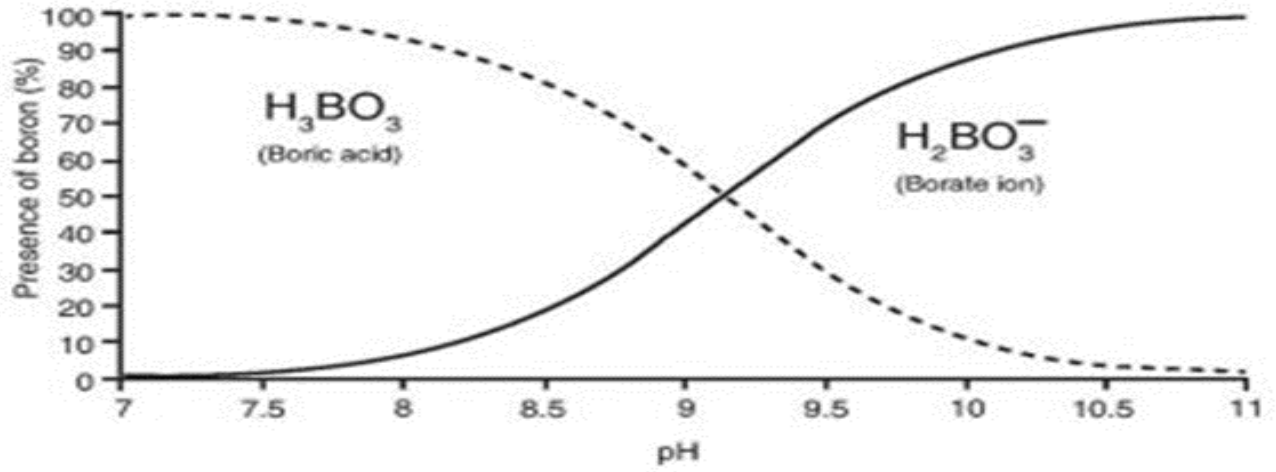

Figure 1. *$H_3BO_3/B(OH)^{4-}$ distribution as a function of pH (Rodarte & Smith, 2014)*

That is, in any liquid system, pH value is the main parameter which determines the ratio of boric acid and borate. At high pH values, predominating ion is, the monovalent borate anion $B(OH)_4^-$, while at lower pHs, predominating one is unionized boric acid $B(OH)_3$ (Atalay Sönmez, 2014).

However, concentration is also an important parameter. The concentration constant (K) of boric acid increases with increasing concentration. If the total boron concentration in the aqueous solution is less than 0.025 M (0.1% B_2O_3 or 270 mg B/L), it is known that only H_3BO_3 and $B(OH)_4^-$ ions are present in the environment. Conversion to polyborates occurs between pH 6-11 and at higher concentrations (>0.025 M). Highly soluble polyborate ions such as $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^-$ and $B_5O_6(OH)_4$ are formed (Atalay Sönmez, 2014).

1.3. Boron in Turkey

73% of the world's boron reserves exist in Turkey. Eskişehir- Kırka, Kütahya-Emet, Balıkesir-Bigadiç and Bursa-Kestelek have known boron deposites (Yiğitbaşoğlu, 2004; Yağmur, 2012). The most abundant boron minerals in terms of reserves in Turkey are tincal and colemanite.

With the 'Law on the Operation of Boron Salts No. 2840', the production, operation and marketing activities of boron mines in Turkey were given to the Eti Mine Works, which was established by Atatürk in 1935 under the name of Etibank. There are four operating directorates within Eti Mine Works: Kırka bor operation directorate-Eskişehir, Emet boron operation directorate-Kütahya, Bandırma boron and acid factories operation directorate-Balıkesir and Bigadiç boron operation directorate-Balıkesir (Tüzün et al., 2019). Figure 2 shows boron minerals extracted in Turkey (Ateş, 2018).

Figure 2. *Bor minerals in Turkey* ***a)*** *tincal,* ***b)*** *colemanite,* ***c)*** *ulexite (Ateş, 2018)*

1.4. The Impact of Boron on Environment

Air, soil and water are affected by boron therefore the effect of boron on water is evaluated as its effect on drinking water and its effect on agricultural water.

Boron occurs naturally in groundwater, also directly effects groundwater. Water filtered from the surface brings boron along with, and consequently, the composition of the groundwater is effected (Aslan, 2020).

Boron can be found in surface waters as an industrial pollutant or as a product of decayed plant materials and agricultural residues (Bilici Başkan & Atalay, 2014). Boron found in surface waters also originates from domestic wastewater (Bilici Başkan & Atalay, 2014; Aslan, 2020). Wastewaters generated during the operation of mines can cause soil and water pollution problems if precautions are not taken to ensure that. Boron concentration in these wastewaters exceeds the acceptable limit or values determined by the legislation, it can harm aquatic creatures or plants if used in agricultural irrigation and can be harmful to people who use them in their diet.

In Turkey, legislation has been created that includes various limits for the discharge of boron in order to protect the environment and also boron intake for human health. In this direction, limits for boron have been determined under three headings in the legislation. These are; "Water pollution control regulation (2004), Wastewater treatment plants technical procedures circular (2010) and Regulation on waters intended for human consumption (2005)". The subject of classification of agricultural irrigation waters according to boron concentration has been determined by wastewater treatment plants technical procedures circular (2010). And according to the Regulation on water for human consumption (2005), the maximum boron concentration allowed in drinking water is 1 mg/L (Bilici Başkan & Atalay, 2014). Boron limit values vary depending on the receiving environment where the wastewater will be discharged. According to the 'Water pollution control regulation (2004)', 500 mg/L (ppm) is the discharge criterion to seawater. And the discharge criterion for wastewaters of factories producing chemical boron compounds is 50 ppm (Ünlü et al., 2013).

1.5. Boron Removal Methods

Different methods are used to remove boron from wastewater and water in order to prevent this pollution and possible damages, to use the water for agricultural purposes, and to eliminate the negative effects of the presence of boron in chemical processes. These are as reported in the study of Liu et al. (2022) as; "Chemical Precipitation and (Electric) Coagulation; Extraction Method; Membrane Processes which include forward osmosis (FO) process, Donnan dialysis (DD) process and membrane distillation (MD) process.; Adsorption Technologies which include adsorbents as activated carbon layered double hydroxides (LDHs), industrial waste materials, natural materials (such as eggshells), metal organic frameworks, and porous aromatic frameworks and other novel materials; capacitive deionization (CDI) process and electro deionization (EDI) process; Integrated Methods as AMF and the combination of the resin method and membrane processes etc." Also the integration methods can be used as: RO separation combined with coagulation, MF/UF combined with adsorption, and complexing membrane filtration (CMF). These methods are considered to be promising techniques since being economically, ecologically profitable (Liu et al., 2022).

A study by Bara and Abba (2025) using nano-magnetite sorbent, at the adsorption section of the hybrid system, the wastewater was subjected to adsorption process for 250 minutes. The removal efficiencies of boron, turbidity, copper, and zinc were 74.39%, at 250 minutes contact time. However, this concentration is still above the standard limit (0.5-1.0 mg/L). Then, a nanocomposite membrane was employed as treatment process for

more efficiency. The boron concentration was significantly reduced to 0.43 mg/L, which is below the standard limit. Finally, it is found that the modified hybrid TiO_2 membrane is effective for boron removal from the wastewater.

Zeytuncu et al. (2023) conducted a study aimed at removing boron from industrial wastewaters and comparing the efficiency of chemical precipitation membrane filtration systems. Chemical precipitation, electrocoagulation and reverse osmosis processes were studied. Poly aluminium chloride (PACl), lime, calcium chloride ($CaCl_2$) and barium chloride ($BaCl_2$) and hydrogen peroxide as oxidant were used chemical precipitants. The study found that when solution pH was adjusted at 10, boron removal increased to 99.5%. With application of electrocoagulation, 45% of B were removed from spring water. Boron-removal increased 98% by increasing pH up to 10. DP-SWRO membranes system at pH 10 was found to be the best system. In summary, a hybrid membrane process which contains an electrocoagulation process as a pre-treatment method and a double pass RO membrane system is a very effective process for boron removal.

Bilen et al. (2018) reports that, in studies conducted with reverse osmosis, the removal efficiency was found to be 63-82% on average, and it was seen that the efficiency reached was 99% by increasing the pH to 10.5. In the reverse osmosis method, issues such as membrane stability, cost and coating of the membrane with $CaCO_3$ raise questions about the effectiveness of the method. In addition, this method produces a dirtier waste stream and its disposal poses a separate problem. Boron removal by electro-dialysis method has given partially successful results in synthetic solutions with low boron concentrations. However, due to the high boron concentration in real solutions, high conductivity and the effects of other ions, its application area is quite limited and it is generally used as the final treatment unit in the clean output streams of reverse osmosis treatment processes. In ion exchange studies, boron removal efficiencies in the range of 90-98% have been achieved, but there is an important problem in this method as the regeneration cost. Electrocoagulation has properties as low amount of sludge (compared to chemical coagulation), not giving extra anions to the solution (compared to chemical coagulation) and boron removal with high efficiency. This method is effective at high boron concentrations. Although these advantages are valid for synthetic solutions, this advantageous situation disappears in real solutions. Due to its high energy consumption, it is not appropriate for boron removal, especially in industrial applications. On the other hand, with its simple, industrially easy installation, wide application area and the usability of the boron-containing solid waste resulting from precipitation as raw material in the cement and ceramic industries, the chemical precipitation method is a useful process for boron removal (Bilen et al., 2018). Using hydroxyapatite, lime, and aluminium sulphate in the chemical precipitation process, 99.4% removal efficiency can be reached. Waste generation, high price, and problem with ultimate disposal are the disadvantages of these processes (Fadaei, 2022). Akkurt et al. (2022) stated in their study that as follows: “Eti Maden Kırka boron operations’ wastewater that contained 2752 ppm boron was investigated for boron removal using $Ca(OH)_2$ in the precipitation. The effect of pH and the amount of boron was studied.

It was found that the most important parameter was pH effect. And after adjustment of pH, addition of $Ca(OH)_2$ improved the precipitation. The best result was obtained in the two-stage addition of $Ca(OH)_2$ with the initial control of pH and in the second stage with additional use of aluminium sulphate. Under these conditions, boron content in the wastewater was lowered to 250 ppm". Also Bilen et al. (2018) stated in their study that as follows: "In the literature, general information can be found on the selection of the appropriate treatment process depending on the amount of boron contained in boron-containing water. In studies, in cases where the amount of boron oxide (B_2O_3) is more than 25 g/L (B>7850 mg/L), it is recommended to remove boron by forming low-solubility salts with substances such as $Ca(OH)_2$, MgO, $(NH4)_2CO_3$, Na_2CO_3. It is mentioned that M(OH)n, M: Al, Fe, Sn, Ti, Mn, Ni, Mg, Zn, Zr etc. sorbents or ion exchange resins can be used for boron removal in the situation when the amount of boron oxide (B_2O_3) is between these values as; 315<B<1000 mg/L. Finally, in cases where the amount of B_2O_3 is less than 1 g/L (B<315 mg/L), boron can be removed with various membrane or electrochemical methods according to the recent studies."

For removing boron from water and wastewater, there is no simple method (Zincir, 2013). Therefore, in ongoing projects around the world, an economical method is still sought for the removal of boron. One of the methods used for this purpose has been adsorption due to its ease of application (Zincir, 2013). Adsorption is one of the most versatile and widely used purification methods recently (Zincir, 2013). Adsorption is effective for many natural biological and chemical systems and is used in industrial applications to purify wastewater and drinking water.

However, attempts to carry out treatment with known adsorbents cause wastewater treatment costs to increase. For this reason, many researchers have directed their studies to cheap and abundant adsorbents (Zincir, 2013). Evaluating natural waste adsorbents is important from an environmental and economic perspective. In fact, some adsorbents used in boron removal can be regenerated and reused (Ateş, 2018). In addition, some adsorbents (meerschaum and alumina) are added to the cement together with the boron they adsorb, thus preventing used adsorbents that are not regenerated from creating new boron pollution (Ateş, 2018).

Bhagyaraj et al. (2021) stated in their study that as follows: "Using waste-derived materials is highly significant for boron removal according to economic advantages. To determine boron adsorption performance; rice, walnut shells, wheat, various seeds, eggshells, and eggshell membrane, palm seed ash have been studied. At neutral pH, with a minor effect of reaction time and temperature on the adsorption process, the boron removal efficiency of the ash was found to be 46%. Maximum adsorption capacity of 4.23 mg/g B/L was obtained with the use of rice husks."

Liao et al. (2024) stated in their study that as follows: "Modified sugarcane bagasse was used for adsorption studies. The optimum conditions were with 5 ppm $MgCl_2$ addition at pH 9 according to the drinking water quality standards. The maximum boron adsorption capacity was 36 mg per 1 g char. Data fitted to Langmuir adsorption isotherm." That study was carried out with synthetically prepared boron solution.

Çelebi (2020) stated in his study that as follows: “In this study, the adsorption capacity of natural pumpkin seed shell was investigated. For the study, the effect of pH of the solution, pumpkin seed shell concentration and contact time on the adsorption process were evaluated under a constant mixing speed (150 rpm) and temperature (20 ºC). Optimum conditions for adsorption were determined as adsorbent dose as 2 g/L, pH as 5.13 and contact time as 5 minutes. The maximum boron treatment efficiency of the pumpkin seed shell was obtained as approximately 88% under ideal conditions. The maximum adsorption capacity based on Langmuir isotherm is 12.61 mg/g and the adsorption of boron on pumpkin seed shell is defined by pseudo-second-order kinetic. As a result, it was noted that the boron element can be effectively removed from the aqueous solution using pumpkin seed shell.” That study was carried out with synthetically prepared boron solution having 1000 mg/L boron value.

Liu et al. (2022) stated in their study that as follows: “Natural materials have obvious advantages in relation to their sources and prices. Natural materials, such as bentonite, kaolinite, zeolite, waste calcite, wheat, rice, and walnut green shell were used in literature studies. The best performance was obtained with waste calcite and rice residue. Generally, organic adsorbents showed a higher boron adsorption capacity than mineral adsorbents. And also Liu et al. (2022) stated in their study that waste eggshells can also be used to remove boron. And also Liu et al. (2022) stated as follows: “Researchers have found that waste eggshells can also be used to remove boron successfully. This good boron adsorption capacity was attributed to the calcium oxide formed after the eggshell’s calcination, which not only adjusts the pH of water but also reacts with borate ions”.

Saleh Al-dhaw et al. (2023) stated in their study that as follows: “CRB05 was used as an adsorbent for boron removal from a synthesized solution. On boron removal, the effects of adsorbent dosage, contact time, boron concentration, and pH were investigated. It was found that pH was very important on boron removal. 98% removal was achieved with at pH 4.5, adsorbent dosage 1125 mg/L, time 255 minutes and concentration 1150 mg/L. And it was concluded that CRB05 is an effective adsorbent for boron removal from synthetic boron solutions”.

Öcal et al. (2024) stated in their study as follows: “By using different methods such as ion exchange resins, membrane processes and adsorption, boron removal has been studied from wastewater. With high operational costs, most of this methods produce excessive waste unfortunately. So, for purification of wastewater containing high concentrations of boron, more sustainable methods are required. In this study, a sustainable treatment process was developed for wastewater containing high concentrations of boron. This study investigated the removal of boron from wastewater by using $Al(OH)_3$ as an adsorbent. The main goal of the study was the reuse of adsorbent ($Al(OH)_3$) and the potential recovery of boric acid. It was seen that although lower concentrations of boron were obtained at pH 10.5 (980 mg/L and 635 mg/L at pH of 9.0 and 10.5, respectively), the amount of adsorbed boron at pH 9 was substantially higher (94.7 mg B/g $Al(OH)_3$ and 27.8 mg B/g $Al(OH)_3$ at pH of 9.0 and 10.5, respectively). This was attributed to the higher initial boron

concentrations and the formation of boric acid and polyborate complexes at pH 9.0. According to these results, polyborate species sorption was an outer sphere complex formation, which led to the desorption of boron as pH lowered. Adsorbed boron species to $Al(OH)_3$ could effectively be desorbed at low pH values (pH<5.0); which allows $Al(OH)_3$ to be used in successive adsorption studies. Approximately 55% of boron recovery from pre-treated wastewater was possible with the effective reuse of adsorbent. Based on the amounts of chemical consumptions and boron recovery, a net profit of 2.85 \$/m^3 could be obtained."

Although boron has important micronutrient properties, it has harmful effects when taken in high doses. As a result, although boron is necessary, too much of it has a poisonous effect for living things. So, the importance of keeping the amount of boron in various water resources under control and removing boron from wastewater becomes evident.

Therefore, in this study, it is aimed to conduct studies on the removal of boron in wastewater taken from the Emet boron operations directorates affiliated to Eti Mine Works to determine the best removal method using natural and modified adsorbents and to reveal the relationship that represents the experimental data. In the studies in the literature, generally synthetically prepared boron solutions were used. Therefore, this study conducted with industrial wastewater makes it specific. Unlike the methods used in Eti Mine, the adsorption method was also tried to reduce the boron concentration in industrial boron waters below the regulation limit values of Turkey. Also carrying out adsorption with waste natural materials for purifying original boron water is also important in the sense of contributing these materials to the economy and for environmental protection. This also makes this study specific.

2. MATERIAL AND METHOD

2.1. Adsorption and Chemical Precipitation with Emet Boric Acid Factory Waste Dam

In the first part of study for adsorption studies, waste clays were obtained from Emet, Bandırma, Kırka, Bigadiç boron operations directorates. Clays were ground and 2 g of clay sample was used as adsorbent. And zeolites which exist at Bigadiç operations directorates site were obtained. The zeolites were crushed in a jaw crusher and sieved in a vibrating sieve and classified according to grain size as a result of sieve analysis. The fractionated zeolite samples were as; D>1mm, D<0.125, D<0.50 and indexed as 1, 2, 3 respectively. In adsorption experiments 2 g of zeolite was used.

In addition, walnut shells, waste corn cobs and waste sunflower were also used in adsorption studies as natural waste adsorbents in the study.

First of all, walnut shells were broken, ground, sieved in a vibrating sieve and separated into fractions.

Two different acids, HCl and H_2SO_4, were used to modify walnut shells. Ground walnut shells with +500 μ fraction were divided into two equal parts by weight and kept separately in 250 mL 0.1 M HCl and 250 mL 0.1 M H_2SO_4 solution for 24 hours. Then, they were filtered, washed with pure water, filtered again and then

heated at 110 °C. They were dried in the oven for 3.5 hours. The reason for choosing the +500 µ size was to repeat the adsorption process with other smaller sized walnut shells if successful removal was not achieved with this particle size. 2 g of ground walnut shells activated with HCl and H_2SO_4 were used. The aim was to understand whether the interaction with acid will had a positive contribution to adsorption. Also to understand which acid had positive effect. Studies continued with pH adjustment to see the effect of pH on adsorption. Adsorption studies were carried out in wastewater at different pH values (2,7,9,11). The pH of the initial boron wastewater was 4. 2 g of HCl-treated ground walnut shells (+500 µ) were used. Afterwards, in order to understand the effect of adsorbent amount on adsorption, adsorption studies were carried out in wastewater at pH 9 as a result of pH adjustment. 2 g and 4 g of HCl-activated ground walnut shells (+500 µ) were used.

Then waste corn cobs and waste sunflower were also used in adsorption studies. Waste corn cobs and waste sunflower stems were ground and divided into sections, treated with 0.1 M HCl and 0.05 M NaOH and kept for a 24 hours. Afterwards, they were filtered and washed with pure water, dried in the oven at 110 ºC for 3.5 hours and made ready for adsorption.

2 g of waste corn cobs and waste sunflower stems were used.

2.1.1. Adsorption Studies with Emet Boric Acid Factory Waste Dam

Boron removal from the wastewater taken from the Emet boric acid factory waste dam was carried out. This wastewater had 5883 ppm boron value. The boron amount was determined according to the B_2O_3 analyse method used at Eti Mine Works according to the method in B_2O_3 Analyse Book (Eti Mine Works Quality Management System). pH was adjusted to 7.60 with 0.5 N HCl and 0.5 N NaOH. Afterwards, 5 g of mannitol added to the solution and the solution was titrated with 0.5 N NaOH until pH reaches 7.60. The amount of B_2O_3 was calculated from the consumption of NaOH. The amount of B_2O_3% (A) is calculated as a weight percentage with the formula below.

$$A = [V \times O,017405 \times 100 \times f] \div m \quad (2)$$

Here; V: volume of sodium hydroxide solution spent in the titration after adding mannitol to the solution, mL; m: weight of the test sample, g; f: titration factor, 0.017405: Amount of B_20_3 corresponding to 1 mL of 0.5 N NaOH. The elemental percentage [%B] of the test sample is calculated with the formula below.

$$\%B = \%B_2O_3 \div 3.22 \quad (3)$$

All adsorption studies were studied in batch system and carried out at 25 ºC in a water bath for 2 hours with 170 rpm rapid mixing speed according to evaluation of the literature values (Öztürk & Kavak, 2004; Sütçü, 2005; Karahan et al., 2006; Liu et al., 2009; Bhagyaraj et al., 2021; Çelebi, 2020; Liao et al., 2024). 100 mL boron wastewater was used. Different amounts of adsorbents were used and different pH values were studied to see the effect of adsorbent amount and pH. Also effect of particle size was studied. Then, the samples were

filtered through blue striped filter paper and the filtrate was analysed by titration method, mentioned above, for boron analyses.

However, for zeolite adsorption, 1 hour; 1 hour and 45 minutes; 2 hours were also tried.

2.1.2. Chemical Precipitation with Emet Boric Acid Factory Waste Dam

In the second part of study, it was thought that it would be more appropriate to remove some of the boron in wastewater, having high boron content, by chemical precipitation with lime (Bilen et al., 2018) as a preliminary process in the removal of boron from wastewater and then to continue the removal by adsorption using environmentally friendly natural adsorbents. Boron removal from the wastewater taken from the Emet Boric Acid Factory Waste Dam was carried out, having 5883 ppm boron value, in a temperature-controlled magnetic stirrer heater a rotation speed of 760 rpm according to the literature values evaluation (Kökkılıç, 2003; Ateş, 2018; Bilen et al., 2018) at different temperatures as 25 ºC, 55 ºC and 88 ºC. The wastewater sample had a value of 5883 ppm and the amount of boron in it was 5.83 g/L. For 200 mL water samples, studies were carried out with 1,5; 3, 6, 15, 30 g of lime. 1 hour working time, 1 hour waiting time were applied. Then, the samples were filtered through blue striped filter paper and the filtrate was analysed by titration method mentioned above to determine boron value left.

2.2. Chemical Precipitation and Adsorption with Espey Spring Water(a)

2.2.1. Chemical Precipitation with Espey Spring Water(a)

The spring waters with high boron content in the Espey open pit site belonging to the Emet boron operations directorate of Eti Mine Works, feed the Gelenbek stream in the region. This high boron content water is connected to the Susurluk basin in the following regions, negatively effecting the irrigation water quality of the basin. Since Espey Spring Water had high boron content (4590 ppm), removal of boron from this water was studied in the framework of social responsibility. Three different amounts of lime were added (5, 10, 20 g) to 200 mL Espey Spring Water samples. Studies were carried out in a temperature-controlled magnetic stirrer heater at a temperature of 25 ºC and a rotation speed of 760 rpm according to boric acid factory wastewater studies mentioned above and the literature values evaluation (Kökkılıç, 2003; Ateş, 2018; Bilen et al., 2018). 1 hour working time, 1 hour waiting time were applied. Then, the samples were filtered through blue striped filter paper and the filtrate was analysed by titration method mentioned above to determine boron value left.

2.2.2 Adsorption with Espey Spring Water(a)

Afterwards, adsorption studies were carried out. 0.1 M HCl treated walnut shells were tried firstly. 2 g and 4 g of walnut shells were used in order to understand the effect of adsorbent amount on adsorption. Then it was decided to continue to the studies by adjusting pH. According to the former studies carried out with walnut shells in the scope of this study, pH was adjusted to 9. For adsorption, walnut shells in +500 μ fraction treated with 0.1 M HCl were used. 2 g and 4 g of walnut shells were used. In order to understand the effect of particle

size on adsorption, the remaining walnut shells were ground and sieved. The walnut shells in the -63 µ fraction, which are called under-sieve, were treated with 0.1 M, 37.5% HCl for a period of 24 hours. During filtration with a vacuum filter, washing with pure water (was carried out to remove acid. Treated walnut shells were dried in an oven at 110 °C for 3.5 hours. According to the results obtained with 2 and 4 g of walnut shells in the +500 µ fraction activated with 0.1 M HCl and since the amount of substance was low, studies were carried out with 2 g of adsorbent in -63 µ fraction. Afterwards, different pH values were studied to see the effect of pH change on adsorption in Espey Spring Water water to be treated. pH adjustment was performed with 0.1 M, 37.5% HCl and 0.5 M NaOH. The pH values studied were 11.30, which is the pH of the water after acid-treated walnut shell addition, and after pH adjustments as 12; 9; 7 and 4. For adsorption studies, 2 g of -63 µ fraction walnut shells was used.

In order to use a different environmentally friendly adsorbent, the use of almond shells was considered. The almond shells were ground in a grinder, sieved in a vibrating sieve and classified according to particle size as a result of sieve analysis. In order to be similar to the walnut shell study, +500 µ fraction and -63 µ fractions were thought to be used in adsorption studies.

Almond shells in +500 µ fraction were kept in 0.1 M HCl for 24 hours, washed with pure water to remove acid and dried. Different pH values were studied to see the effect of pH change on adsorption in wastewater. pH adjustment was made with 0.1 M, 37.5% HCl. The pH values studied were 12, 9,7 and 4. For adsorption studies, 2 g and 4 of +500 fraction walnut shells were used.

Then, the adsorption process was carried out with almond shells in the -63 µ fraction, which were kept in 0.1 M HCl for 24 hours, washed with pure water to remove acid, and dried. Since there was not enough material for this fraction, the study was carried out with only 2 g. Different pH values were studied to see the effect of pH change on adsorption in wastewater. pH adjustment was made with 0.1 M, 37.5% HCl. The pH values studied were 12, 9,7 and 4.

Afterwards, it was decided to work with wood sawdust, which was a different environmentally friendly adsorbent. First of all, the boron amount of Espey Spring Water, which was previously subjected to chemical treatment and then filtered, was measured. Sawdust that was kept in 0.1 M NaOH for 24 hours and washed with pure water to remove the base then it was dried in the oven for 3.5 hours at 90 °C. 2 g and 4 g of sawdust were used in different adsorption studies to see the effect of amount of adsorbent on adsorption. Adsorption studies with sawdust were carried out by diluting the spring water with pure water at 1/2, 1/5 and 1/10 ratios, as well as with also not diluted pure Espey Spring Water.

All adsorption studies were carried out at 25 ºC in a water bath with 170 rpm rapid shaking for 2 hours. Then, the samples were filtered through blue striped filter paper and the filtrate was analysed by titration method mentioned above. 100 mL Espey Spring Water was used. Adsorption studies were carried out using different amount of adsorbent, pH and particle size to determine the effects of these parameters on adsorption.

Adsorption studies with sawdust were carried out by diluting the spring water with pure water at 1/2, 1/5 and 1/10 ratios with also not diluted pure Espey Spring Water.

Figure 3 shows adsorption studies for 0.1 M HCl treated walnut shells in shaking water bath.

Figure 3. *Adsorption studies with almond shells in a shaking water bath*

2.3. Chemical Precipitation and Adsorption with Espey Spring Water(b)

In the third part of this study, since there was no leftover water before adsorption, Espey Spring Water was brought from Emet again and the amount of boron was measured. Firstly, the stream water was filtered and the boron amount was measured. The boron amount of the water was 3810 ppm.

2.3.1. Chemical Precipitation with Espey Spring Water(b)

That time, studies were conducted with 10 g of lime. 2 hours of working time and 2 hours of waiting time were selected in order to increase boron removal. Studies were carried out in a temperature-controlled magnetic stirrer heater at a temperature of 25 ºC and a rotation speed of 760 rpm according to part *2.2.1 Chemical precipitation with Espey Spring Water(a).* Then, the samples were filtered through blue striped filter paper and the filtrate was analysed by titration method mentioned above to determine boron value left.

2.3.2. Adsorption with Espey Spring Water(b)

Afterwards, waste activated carbon, used in water purification devices, was tried for adsorption studies, which was a different environmentally friendly adsorbent. Waste activated carbon was ground and treated by immersing and maintained it in 0.1 M NaOH for 24 hours. Afterwards, it was filtered and washed with distilled water until drained water pH became 7 and then dried in the oven at 110 ºC for 3.5 hours and made ready for adsorption. In addition, another environmentally friendly adsorbent pine cane was tried for boron removal. Pine cane was ground and treated with 0.1 M NaOH and kept for a 24 hours. Afterwards, it was filtered and washed with distilled water, dried in the oven at 90 ºC, since it being more heat sensitive, for 3.5 hours and made ready for adsorption. All adsorption studies were carried out at 25 ºC in a water bath with 170 rpm rapid shaking for 2 hours. Then, the samples were filtered through blue striped filter paper and the filtrate was

analysed by titration method mentioned above. 100 mL Espey Spring Water was used. In that time in order to increase effectiveness, 10 g of adsorbent was used for both adsorbents and adsorption was carried out in the same time for both adsorbents to acquire better results.

Adsorption studies were continued with almond shells used in part *2.2.2 Adsorption with Espey Spring Water (a)* in order to be compatible with the studies of this part. For almond shells; the effect of the amount of adsorbent as 2, 4, 8, 10, 20 g; the effect of pH as 4, 7, 10, 11, 12; the effect of mixing speed as 120, 150, 170, 180, 200 rpm, the effect of temperature as 15 ℃, 25 ℃, 40 ℃, 55 ℃, 70 ℃ and effect of time as 1, 2, 3, 4, 5 hours were studied to see the effect of these parameters on adsorption efficiency. All adsorption studies were carried out at in the shaking water bath. 100 mL Espey Spring Water was used.

3. RESULTS AND DISCUSSION

3.1. Adsorption and Chemical Precipitation with Emet Boric Acid Factory Waste Dam

3.1.1. Adsorption Studies with Emet Boric Acid Factory Waste Dam

The results of adsorption studies which were carried out with waste clays (obtained from Emet, Bandırma, Kırka, Bigadiç operations directorates and indexed as 1,2,3,4,5 respectively) are shown in Table 1.

Table 1. *Adsorption results using clay samples*

Clay Samples	B_2O_3 [g/L]	B_2O_3 [ppm]	B [g/L]	B [ppm]
1	19.307	19,307	5.994	5994
2	35.736	35,736	11.098	11,098
3	56.802	56,802	17.642	17,642
4	40.976	40,976	12.725	12,725
5	278.682	278,682	86.547	86,547

The results in Table 1 indicates that, the desired boron removal efficiency could not be achieved in studies conducted with clays. Comparison of initial (5883 ppm) and final boron contents of wastewater indicates an increase in the boron content of the wastewater. This phenomenon can be explained as follows.

According to these results, the desired boron removal efficiency could not be achieved in studies conducted with clays considering the initial boron value of wastewater was 5883 ppm. There was an increase in the amount of boron in the water compared to the initial value.

Baran (2014) have mentioned the following studies as follows: “Keren et al. (1981) and Karahan et al. (2006), montmorillonite, kaolinite, illite, sepiolite, bentonite and their modified forms with nonylammonium chloride were used as adsorbents for boron removal. In these studies, experiments were carried out using initial boron concentrations of 1-50 mg/L. As a result of batch system studies, it was observed that the boron retention capacity of modified clay surfaces was higher than that of unmodified clay mineral”.

As reported by Seyhan et al. (2007), iron-rich Çamlıca bentonites CB1, CB2 were used for boron removal from water. Boron was determined by the fluorimetric-azomethin-H method, which is a new method. Using the factorial design method, the optimum conditions were found to be 0.250 g clay and 20 mL sample at pH 10, 45 ◦C. Under these conditions, boron removal is 80% for CB1 and 30% for CB 2. This high removal value can be due to the lower boron values of boron water and clay used was not saturated with boron.

As mentioned above, in these previous studies boron values in water are in low amounts. However, in this study boron in water was very high (5883 ppm). Also the increase in boron concentration after adsorption according to the Table 1, can be explained by the release of boron during adsorption from clay minerals that extracted from the same mine and therefore saturated with boron. The results of adsorption studies which were carried out by using natural zeolite as adsorbent are shown in Table 2-3-4.

Table 2. *Adsorption results using natural zeolite for 1 hour*

Zeolite Samples	B_2O_3 [g/L]	B_2O_3 [ppm]	B [g/L]	B [ppm]
1	18.677	18,677	5.800	5800
2	18.588	18,588	5.773	5773
3	18.588	18,588	5.773	5773

Table 3*. Adsoption results using natural zeolite for 1 hour and 45 minutes*

Zeolite Samples	B_2O_3 [g/L]	B_2O_3 [ppm]	B [g/L]	B [ppm]
1	18.659	18,659	5.795	5795
2	18.552	18,552	5.761	5761
3	18.570	18,570	5.767	5767

Table 4. *Adsorption results using natural with zeolite for 2 hours*

Zeolite Samples	B_2O_3 [g/L]	B_2O_3 [ppm]	B [g/L]	B [ppm]
1	18.659	18,659	5.795	5795
2	18.552	18,552	5.761	5761
3	18.570	18,570	5.767	5767

In studies conducted with 3 different fractions of zeolite over different time periods, it was seen that time and particle size changes did not have a significant effect on the amount of adsorption and most importantly, the amount of boron in the wastewater after adsorption was still at very high levels. As a result of the boron-rich zeolite found in the same area with boron in the boron local soils, it was thought that it did not have sufficient capacity in terms of boron adsorption, and to use a new adsorbent, walnut shell was decided.

Also, Yüksel and Yürüm (2009) also stated that for boron removal, while natural zeolite (clinoptilot) and demineralized lignite were not successful, 90% boron was removed by using fly ash.

Adsorption results which were carried out with Walnut Shell Particles Treated with HCl and H_2SO_4, (+500 µ) are shown in Table 5.

According to these results, the amount of boron remaining in the water showed that the effect of both acid-treated walnut shells on the adsorption efficiency was almost the same. Considering that the initial boron concentration in water was 5883 ppm, as can be seen from Table 5, an efficient adsorption result was not achieved unfortunately.

Adsorption Results which were carried out with HCl activated walnut shell Particles at different pH's, (+500 µ) are shown in Table 6.

Table 5. *Adsorption results using walnut shell particles treated with HCl and H_2SO_4, (+500 µ)*

pH	B_2O_3 [g/L]	B_2O_3 [ppm]	B [g/L]	B [ppm]
2	18.340	18,34	5.696	5696
7	17.774	17,774	5.520	5520
9	16.731	16,731	5.196	5196
11	15.406	15,406	4.784	4784

Table 6. *Adsorption results using HCl activated walnut shell particles at different pH's, (+500 µ)*

	B_2O_3 [g/L]	B_2O_3 [ppm]	B [g/L]	B [ppm]
HCl treated walnut shells	18.818	18,818	5.844	5844
H_2SO_4 treated walnut shells	18.800	18,8	5.839	5839

According to these results, as the pH value increased, the boron removal efficiency from boron-containing wastewater had increased, albeit slightly. However, it should be taken into consideration that as a result of pH adjustment, there was turbidity and precipitation after adsorption in the samples at pH 9 and 11, and that the samples were diluted as the amount added as a result of pH 9 and 11 adjustment was slightly more than the other samples and the total volume exceeded 100 mL. Because of the fact that, the unit of measurement was mg/L, ppm.

Adsorption Results with Different Amounts of Walnut Shell Particles (Activated with HCl) at pH 9, (+500 µ) are shown in Table 7.

Table 7. *Adsorption results using different amounts of walnut shell particles (activated with hcl) at ph 9, (+500 µ)*

Amount of Adsorbent	B_2O_3 [g/L]	B_2O_3 [ppm]	B [g/L]	B [ppm]
2	16.225	16,225	5.039	5039
4	16.102	16,102	5.000	5000

According to these results, considering that the initial boron concentration was 5883 ppm, a small amount of removal was achieved. And as the amount of adsorbent increased at pH 9, the amount of adsorption increased, as seen in Table.7. This was because as adsorbent amount increased, the number of adsorption sites on the adsorbent surface increased.

Due to the inadequacy of walnut shells for boron removal, waste corn cobs and waste sunflower stems were used.

Adsorption Results with (acid/base) treated and untreated waste sunflower stems and waste corn cobs are shown in Table 8.

It can be seen from these results that, output ppm values obtained as a result of the studies were still around 5800. This showed that ground waste corn cobs and ground waste sunflower stems, as well as their acid and base modified forms, were unfortunately insufficient to remove boron from wastewater by adsorption, considering the initial value of the water was 5883 ppm which was a very high boron value.

For this reason, it was thought that it would be more appropriate to remove some of the boron in the wastewater by chemical precipitation with lime as a preliminary process, then to conduct adsorption studies with environmentally friendly natural adsorbents.

Table 8. *Adsorption results using (acid/base) treated and untreated waste sunflower stems and waste corn cobs*

Adsorbent Type	B_2O_3 [g/L]	B_2O_3 [ppm]	B [g/L]	B [ppm]
Waste Sunflower Stems	18.739	18,739	5.819	5819
Waste Corn Cobs	18.896	18,896	5.868	5868
0.1 M HCl treated Waste Sunflower Stems	18.931	18,931	5.879	5879
0.1 M HCl treated Waste Corn Cobs	18.896	18,896	5.868	5868
0.05 M NaOH treated Waste Sunflower Stems	18.896	18,896	5.868	5868
0.05 M NaOH treated Waste Corn Cobs	18.913	18,913	5.864	5864

3.1.2. Chemical Precipitation with Emet Boric Acid Factory Waste Dam

Results of chemical precipitation with different amounts of lime at 55 ºC temperature are shown in Table 9.

It can be seen from these results that the boron removal increased as the amount of lime increased. The reason for this is as explained below.

With the addition of lime to boron wastewater, the pH of the water increased to value of around 11-12. And in this pH range, as explained in the *1. Introduction* part, at high pH's, boron is present in the form of $B(OH)_4^-$ in water. Therefore, the reaction between lime and boron is as follows:

$$2Ca^{+2}{}_{(aq)} + 2B(OH)^-_{4\,(aq)} + 2OH^-{}_{(aq)} \rightarrow Ca_2B_2O_5 \cdot (H_2O)_{(s)} + 4H_2O_{(l)} \quad (4)$$

Table 9. *Results of Chemical Precipitation Study Performed using Different Amounts of Lime at 55 ºC Temperature*

Lime Amount [g]	B_2O_3 [g/L]	B_2O_3 [ppm]	B [g/L]	B [ppm]
1.5	18.861	18,861	5.858	5858
3	16.346	16,346	5.076	5076
6	10.199	10,199	3.167	3167
15	2.480	2480	0.771	771
30	2.235	2235	0.694	694

According to the above reaction, as the amount of lime (Ca^{+2}) increases, the amount of precipitate ($Ca_2B_2O_5.(H_2O)_s$) and the lime surface area that can interact with boron will increase. As a result, the boron removal efficiency from water will increase with the increasing amount of lime.

However, as the amount of lime increases, solution mixing becomes difficult and as the amount of filtrate decreases, sludge formation increases. Therefore, studies were limited to 30 g of lime. According to these results, while boron removal was not sufficient for 1.5 and 3 g lime (0.4% and 13% respectively), it was moderate for 6 g lime (46%); and for 15 and 30 g lime, it is promising and productive with 771 (87%) and 694 (88%) ppm, respectively. Filtration after chemical precipitation with different amounts of lime ($Ca(OH)_2$) at 55 ºC can be seen from Figure 4.

Studies were continued at 25 ºC to see the effect of temperature on precipitation with lime. Since the study at 1.5 and 3 g of lime by mass was insufficient at 55 º C, studies at 25 ºC were conducted by using higher amount of lime.

The results of chemical precipitation with different amounts of lime at 25 ºC temperature are shown in Table 10.

It can be seen from Table 10 that, as the amount of lime increased, the boron removal increased (about 49 ppm, although there is a slight difference between 6 and 15 g). While the boron removal in the work done with 6 g to 15 g of lime was very low (almost no removal), the work done with 30 g lime could be considered as moderately efficient with 55% removal.

Figure 4. *Filtration After Chemical Precipitation with Different Amounts of Lime at 55 ºC*

Table 10*. Results of chemical precipitation study performed using different amounts of lime at 25 ºc temperature*

Lime Amount [g]	B_2O_3 [g/L]	B_2O_3 [ppm]	B [g/L]	B [ppm]
15	0.593	593	0.184	184

Studies were continued at 88 ºC to see the effect of temperature on precipitation with lime. The amount of lime to be worked at 88 ºC was based on the amount of lime worked at 55 ºC, as the results of the study at 55 ºC were more efficient than 25 ºC. And since 1.5 and 3 g were insufficient in the studies carried out at 55 ºC, and 30 g could cause more sludge formation, the amount of lime to be worked at 88 ºC was chosen as 15 g. The results obtained are presented in Table 11.

Table 11. *Results of chemical precipitation study performed using lime at 88 ºc temperature*

Lime Amount [g]	B_2O_3 [g/L]	B_2O_3 [ppm]	B [g/L]	B [ppm]
6	18.966	18,966	5.890	5890
15	18.809	18,809	5.841	5841
30	8.453	8453	2.625	2625

According to this result; 184 ppm was a very efficient result with 97% removal.

In order to better understand the effect of reaction temperature on boron removal, it is first necessary to determine whether the reaction between lime and boron (Equation 4), given above, is exothermic or endothermic. The ΔH calculation for this reaction at 298 K is made below according to the values shown in Table 12 using Equation 5 and Equation 6 *(Bilen et al., 2018)*.

Table 12. *Enthalpies of reactants and products at 298 k (bilen et al., 2018)*

Ion	ΔH_{298} (kJ/mole)
Ca^{+2}	-542.83
$B(OH)_{4-(aq)}$	-1344.03
$OH^{-}_{(aq)}$	-229.99
$Ca_2B_2O_5{\bullet}(H_2O)_s$	-3041.80
$H_2O_{(l)}$	-242.00

$$(\Delta H)_{298} = \left[1 \times \Delta H_{Ca_2B_2O_5\cdot(H_2O)_{(s)}} + 4 \times \Delta H_{4H_2O_{(l)}}\right] - \left[2 \times \Delta H_{Ca^{+2}{}_{(aq)}} + 2 \times \Delta H_{B(OH)^{-}_{4\,(aq)}} + 2 \times \Delta H_{OH^{-}{}_{(aq)}}\right] \quad (5)$$

$$(\Delta H)_{298} = [1 \times (-3041.80) + 4 \times (-242.00)] - [2 \times (-542.83) + 2 \times (-1344.03) + 2 \times (-229.99)] = 223.90\ \text{kJ/mole} \quad (6)$$

The (ΔH) value of 223.90 kJ/mole shows that the reaction between $Ca(OH)_2$ and boron is endothermic and the reaction will shift towards the products as the temperature increases. According to this, in this study, it is an expected result that the amount of precipitated matter increases with the increase in temperature.

Considering the literature, Selimoglu and Boncukoğlu (2019) studied boron removal from synthetically prepared boron solutions by chemical precipitation with lime. It was concluded that by increasing the temperature and the amount of $Ca(OH)_2$, boron removal increased. And the removal achieved was 98%.

In summary, regarding the studies carried out, in order to remove boron from the wastewater of Emet boron operations directorate waste dam with high boron content, since the adsorption process carried out with environmentally friendly adsorbents were unsuccessful, chemical precipitation with lime ($Ca(OH)_2$) was used as a pre-treatment, and efficient results were obtained with chemical precipitation process as 97% of removal.

3.2. Chemical Precipitation and Adsorption with Espey Spring Water(a)

3.2.1. Chemical Precipitation with Espey Spring Water(a)

Since efficient results were obtained with the chemical precipitation method using lime ($Ca(OH)_2$) for the removal of boron from the wastewater of the Emet boron operation directorate waste dam, the studies for the purification of Emet Espey Spring Water continued with chemical precipitation as a pre-treatment in this study period as well as purification of Emet boron operation directorate waste dam wastewater. It was aimed to continue the work with the treatment of spring water by adsorption, which would be obtained with optimum values to be reached.

The initial boron value of Emet Espey Spring Water, which feeds Gelenbek stream, was 4590 ppm and the pH was 6.86.

To remind that, efficient results were obtained with chemical precipitation for the removal of boron from the wastewater of the Emet boron operation directorate waste dam at 88 ºC and 55 ºC. Chemical treatment was continued at 25 ºC because of the fact that practically working at high temperatures creates energy costs in applications temperatures and will indirectly harm the environment (fossil fuel use, etc.).

Results of chemical precipitation study of Espey Spring Water, conducted with different amounts of lime at 25 ºC temperature are shown in Table 13.

Table 13. *Results of chemical precipitation study of Espey Spring Water, conducted with different amounts of lime at 25 ºC*

Lime Amount [g]	B_2O_3 [g/L]	B_2O_3 [ppm]	B [g/L]	B [ppm]
5	1.366	1366	0.424	424
10	1.297	1297	0.403	403
20	1.210	1210	0.376	376

It can be seen from Table 13 that, changing the amount of lime did not have much effect on the removal, and 5 g would be sufficient for treatment. Because as the amount of lime increased, the amount of sludge, which was the waste produced as a result of chemical precipitation, would also increase. This was a negative situation for the environment in water treatment. The decrease from 4590 ppm to 424 ppm with 91% percentage removal could be considered as a very good result in terms of chemical treatment with lime. The boron value of this output water was 424 ppm and its pH was 11.67.

3.2.2. Adsorption with Espey Spring Water(a)

Afterwards adsorption studies were carried out. The adsorption results of Espey Spring Water with different amounts of walnut shell particles (activated with HCl) for +500 µ particle size at 25 ºC are shown in Table 14.

Table 14*. Adsorption results of Espey Spring Water using different amounts of walnut shell particles (activated with hcl), (+500 µ) at 25 ºC*

Amount of Adsorbent [g]	B_2O_3 [g/L]	B_2O_3 [ppm]	B [g/L]	B [ppm]
2	1.320	1320	0.410	410
4	1.293	1293	0.401	401

Considering that the initial boron concentration was 424 ppm, a slight removal was achieved with output value of 410 ppm for 2 g of adsorbent (%3.3 removal efficiency) and output value of 401 ppm for 4 g of adsorbent (%5.4 removal efficiency). And as the amount of adsorbent increased, the amount of adsorption increased, albeit slightly. This was because as adsorbent amount increased, the number of adsorption sites on the

adsorbent surface increased. However, with these results, it could be considered that boron removal was not sufficient. Because of this, it was decided to continue to the studies by adjusting pH.

According to the former studies carried out with walnut shells in the scope of this study, pH was adjusted to 9. The adsorption results of Espey Spring Water with different amounts of walnut shell particles (activated with HCl) for +500 µ particle size at 25 ºC, at pH 9 are shown in Table 15.

Table 15. *Adsorption results of Espey Spring Water using different amounts of walnut shell particles (activated with hcl), (+500 µ) at 25 ºc, at pH 9*

Amount of Adsorbent [g]	B_2O_3 [g/L]	B_2O_3 [ppm]	B [g/L]	B [ppm]
2	1.246	1246	0.387	387
4	1.219	1219	0.379	379

It can be seen from these results that, considering that the initial boron concentration was 424 ppm, a slight removal was achieved with output value of 387 ppm (9% removal efficiency) for 2 g of adsorbent and an output value of 379 ppm (11% removal efficiency) for 4 g of adsorbent. And as the amount of adsorbent increased, the amount of adsorption increased, albeit slightly. Compared to the previous study without pH adjustment (pH: 11.67), as seen in Table 14, the amount of boron removal from wastewater increased by adjusting the pH to 9.

In summary, for the adsorption studies carried out with HCl activated walnut shells of +500 µ particle size, as the amount of adsorbent increased, a very small decrease was observed. Again, in the study conducted by adjusting the pH of Espey Spring Water to 9, more efficient results were obtained compared to the study with pH 11.67, original pH. This was because, as explained in the above sections, pH is an important parameter effecting the behaviour of water-soluble boron. Boron is present in the form of non-ionized boric acid, H_3BO_3, in water when the pH is less than 7, and behaves as (-) charged borate, $B(OH)_4^-$, at pH values greater than 10.5. At higher pH values, hydroxyl ions compete with (-) ions on the adsorbent surface and (+) charged surfaces turn into (-) charges. This can be considered as the reason for the lower boron removal efficiency in the previous study (pH: 11.67) without pH adjustment.

For +500 µ particle size walnut shells, the highest yield was obtained with 4 g adsorbent at pH 9 with 379 ppm (11% removal efficiency).

In order to understand the effect of particle size on adsorption, studies continued with the walnut shells in the -63 µ fraction. Also different pH values were tried. The adsorption results of Espey Spring Water with 2 g of walnut shell particles (activated with HCl,) for -63 µ particle size at 25 ºC, at different pHs are shown in Table 16.

According these results, with an output value of 346 ppm (18% removal efficiency), the optimum removal pH could be considered as 9 for -63 µ fraction. It could be thought that as the degree of acidity or alkalinity increased, adsorption was negatively affected. Because of that walnut shell particles were modified with HCl, they had a surface with (+) charged. So in this situation, for effective adsorption, the molecule to be adsorbed should have (-) charge. And pH is an important parameter effecting the behaviour of water-soluble boron. When the pH is less than 7, boron is present in water in the form of non-ionized boric acid, H_3BO_3 and at pH values greater than 10.5 behave as, (-) charged borate, $B(OH)_4^-$ as seen in Figure 1. So, in this conditions borate was more favourable for (+) charged surfaces. Ah higher pH' s as 11.30 and 12 as seen in Table 16, the reason for the decrease in boron adsorption was that the hydroxyl ion competed with the (–) ions on the surface of adsorbent. Because at higher pH' s, (+) charged surfaces turned to (-) charge.

Table 16. *Adsorption results of Espey Spring Water using 2 g of walnut shell particles (activated with hcl), (-63 µ) at 25 ºC, at different pHs*

pH	B_2O_3 [g/L]	B_2O_3 [ppm]	B [g/L]	B [ppm]
12	1.307	1307	0.406	406
11.30	1.289	1289	0.400	400
9	1.115	1115	0.346	346
7	1.150	1150	0.358	358
4	1.185	1185	0.368	368

In summary, the results of the two studies on HCL treated walnut shells at the +500 µ fraction (2 g of adsorbent amount) and HCl treated walnut shells at the -63 µ fraction (2 g adsorbent amount) at 25 °C were compared at close pH 's as 11.67 and 11.30. It was observed that when the particle size decreased, the adsorption efficiency increased slightly, as seen from Table 14 and Table 16, from the 410 ppm (+500 µ fraction) (3.3% removal efficiency) and 400 ppm (-63 µ fraction) (5.6% removal efficiency) values. Because of as particle size decreased, the surface area of adsorbent increased. And because of the fact that resistance to reach pores would be shortening and easier pore diffusion would occur. Decrease in diffusional resistance became.

Then, since adsorption process carried out with walnut shells were unsuccessful, another environmentally friendly adsorbent, almond shells were tried for adsorption studies.

The adsorption results of Espey Spring Water with 2 g of almond shell particles (Activated with HCl), for +500 µ particle size at 25 ºC, at different pHs are shown in Table 17.

The adsorption results of Espey Spring Water with 4 g of almond shell particles (Activated with HCl), for +500 µ particle size at 25 ºC, at different pHs are shown in Table 18.

***Table 17**. Adsorption results of Espey Spring Water using 2 g of almond shell particles (activated with hcl), (+500 µ) at 25 ºC, at different pHs*

pH	B_2O_3 [g/L]	B_2O_3 [ppm]	B [g/L]	B [ppm]
12	1.117	1117	0.347	347
9	1.064	1064	0.330	330
7	1.134	1134	0.353	353
4	1.134	1134	0.353	353

***Table 18**. Adsorption results of Espey Spring Water using 4 g of almond shell particles (activated with hcl), (+500 µ), at 25 ºC, at different pHs*

pH	B_2O_3 [g/L]	B_2O_3 [ppm]	B [g/L]	B [ppm]
12	1.099	1099	0.341	341
9	1.046	1046	0.325	325
7	1.099	1099	0.341	341
4	1.117	1117	0.347	347

When the remaining boron values after adsorption in wastewater at different pHs were evaluated, considering that the initial boron concentration was 424 ppm, it was seen that a small amount of boron removal was achieved.

Comparison of results given in Table 17 and 18 showed that the boron removal increases with the increasing amount of adsorbent. This may be explained by the increasing surface area and consequent increase of active sites available for adsorption with the increasing amount of adsorbent.

The optimum removal pH was determined as 9 for almond shells for +500 µ fraction activated with 0.1 M HCl as output value 330 ppm (for 2 g adsorbent) (22 % removal efficiency) and as output value 325 ppm (for 4 g adsorbent) (23 % removal efficiency). That was because of the reason explained for results discussion of Table 16.

Then, the adsorption process was carried out with almond shells in the -63 µ fraction to see the effect of particle size on adsorption. Adsorption results of Espey Spring Water with 2 g of almond shell particles (activated with HCl), for -63 µ size at 25 ºC, at different pHs are shown in Table 19.

It can be seen from these results that, when the remaining boron values after adsorption in Espey Spring Water at different pHs were evaluated, considering that the initial boron concentration was 424 ppm, a small amount of boron removal was achieved. The optimum removal pH was 9 with output value as 324 ppm (23.5% removal efficiency). That was because of the reason explained for the discussion of results given in Table 16.

Table 19. *Adsorption results of Espey Spring Water using 2 g of almond shell particles (activated with hcl), (-63 µ) at 25 ºC, at different pHs*

pH	B_2O_3 [g/L]	B_2O_3 [ppm]	B [g/L]	B [ppm]
12	1.077	1077	0.334	334
9	1.042	1042	0.324	324
7	1.095	1095	0.340	340
4	1.112	1112	0.345	345

Comparison of the results given in Table 17 (+ 500 µ) and Table 19 (- 63 µ), showed that, when the particle size decreased, the adsorption efficiency increased. Because of as particle size decreased, the surface area of adsorbent increased. Also decrease in particle size causes decrease in diffusional resistance due to the shortened path to reach the active sites interior parts of the adsorbents through the pores. This implies that the adsorption of boron having a diffusion resistance controlling mechanism.

Then, another environmentally friendly adsorbent, saw dust was tried for adsorption studies. First of all, the concentration of boron in Espey Spring Water, which was previously subjected to chemical treatment and then filtered, was measured. The boron value of water was 404 ppm. The reason for the decrease from 424 ppm to 404 ppm in spring water was due to calcium borate precipitation formed at the bottom of Espey Spring Water over time. The adsorption results of Espey Spring Water by using 2 g of saw dust at 25 ºC, at different dilution rates are shown in Table 20.

Table 20. *Adsorption results of Espey Spring Water using 2 g of saw dust at 25 ºC, at different dilution Rates*

Dilution Rate	B_2O_3 [g/L]	B_2O_3 [ppm]	B [g/L]	B [ppm]
0	1.233	1233	0.383	383
1.Feb.	0.616	616	0.191	191
1.May.	0.205	205	0.064	64
1.Oct.	0.120	120	0.037	37

It can be seen from these results that, the amount of boron remaining in the wastewater after the adsorption experiment carried out under the same conditions but without dilution, was 383 ppm. The boron removal achieved was 21 ppm (5.2% removal efficiency), which is much higher than the discharge upper limit value specified in the wastewater regulation of Turkey. For this reason, it was decided to carry out adsorption experiments by diluting the Espey Spring Water.

After adsorption using 1/2 diluted Espey Spring Water, the boron concentration remaining in the wastewater was found to be 191 ppm. With dilution, the initial boron concentration in wastewater, which was 202 ppm before adsorption, decreased to 191 ppm. In other words, 11 ppm (5.4% removal efficiency) removal was

achieved. Since it was observed that boron removal increased with dilution, it was decided to conduct adsorption studies by increasing the dilution rates.

After adsorption using 1/5 diluted Espey Spring Water, the boron concentration remaining in the wastewater was found as 64 ppm. Considering that the initial boron concentration with dilution was 81 ppm, it could be seen that 17 ppm (26.6% removal efficiency) boron removal was achieved by adsorption.

After adsorption using 1/10 diluted Espey Spring Water, the remaining boron concentration in the wastewater was found as 37 ppm. Considering that the concentration of wastewater before adsorption as a result of dilution was 40 ppm, 3 ppm (7.5% removal efficiency) boron removal was achieved via adsorption.

When all results were evaluated for 2 g adsorbent, boron removal was achieved, albeit slightly, as a result of adsorption. The reason for this could be explained by the fact that sawdust is a material with a porous cellulosic structure and complexation with the hydroxylic, carboxylic and phenolic groups in its structure. In addition, it could be mentioned that treatment with NAOH had a positive contribution to adsorption in terms of removing impurities in the adsorbent and allowing easier access of boron to the pores.

As explained in the literature, concentration is an important parameter effecting the behaviour of boron in water. The concentration constant (K) of boric acid increases with increasing concentration. It is known that if the total boron concentration in aqueous solution is less than 0.025 M (0.1% B_2O_3 or 270 mg B/L), only H_3BO_3 and $B(OH)_4^-$ ions are present in the environment. At higher concentrations (>0.025 M), polyborate ions such as $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^-$ and $B_5O_6(OH)_4^-$ are formed.

The reason for the positive effect of dilution on adsorption is that, only H_3BO_3 and $B(OH)_4^-$ ions present in water at low concentrations; whose adsorption is easier than large molecules such as polyborates,

These results showed that boron removal increases with dilution up to a certain dilution, but beyond this dilution ratio, boron removal started to decrease again. In short, it was observed that there was an optimum dilution ratio for boron removal. The reason for this is related to the theorem that as the boron concentration decreases, the driving force for the adsorption decreases.

Based on these results, it could be concluded that the active area of the adsorbent might be insufficient at high boron concentrations, in other words, since all active areas were occupied by boron, the adsorption phenomenon reached a dynamic equilibrium and the amount of adsorbent was increased and the adsorption studies were carried out with different dilution ratios. It was decided to repeat adsorption studies for different dilution ratios by increasing the amount of adsorbent in the same conditions.

The studies were repeated for 4 g of adsorbent and the results were given in Table 21.

Table 21. *Adsorption results of Espey Spring Water using 4 g of saw dust at 25 ºC, at different dilution rates*

Dilution Rate	B_2O_3 [g/L]	B_2O_3 [ppm]	B [g/L]	B [ppm]
0	1.182	1182	0.367	367
1/2	0.599	599	0.186	186
1/5	0.171	171	0.053	53
1/10	0.103	103	0.032	32

As a result of the adsorption experiment performed without dilution, the amount of boron remaining in the wastewater is 367 ppm, i.e. 37 ppm (9.2%) boron removal was achieved. This concentration is much higher than the discharge upper limit value specified in the regulations. Therefore, it was decided to carry out the adsorption experiments by using diluted wastewater.

The results of adsorption experiments by using 1/2, 1/5 and 1/10 diluted wastewater showed that, the boron concentration remaining in wastewater are 186 ppm, 53 ppm and 32 ppm respectively. In another words, at these dilution ratios amount of boron removed 16 ppm, 81 ppm, 8 ppm and removal efficiencies are 7.9%, 34.6% and 20% respectively. These results very well confirmed with the adsorption experiments carried out by using 2 g of adsorbent by indicating there is an optimum dilution ratio for adsorption.

Also comparison of results given in Table 20 and Table 21 showed that, as the amount of adsorbent increased, the amount of adsorption increased due to the increase in surface area and hence increase of active sites on it.

When the results of the studies conducted, 0, 1/2, 1/5 and 1/10 dilution ratios by using 2 g and 4 g adsorbent, were compared, 4.0%, 2.5%, 8% and 12.5% excess removal were obtained for the case of 4g adsorbent than the 2 g adsorbent cases. This may be explained by the increase in area and consequently in active sites available for adsorption with the increasing amount of the adsorbent.

Since the positive effect of increasing the amount of adsorbent was seen, it was considered to continue the studies with the increase in the amount of adsorbent.

When the studies about saw dust in literature was considered; Jaouadi (2021) explains the study as follow**,** "Pinewood sawdust is a good precursor for activated carbon production. Activated carbon was prepared from sawdust by chemical activation using H_3PO_4 at 300°C. Sawdust and activated carbon were investigated as bio-adsorbents for boron removal from freshwater. Sawdust showed the highest boron adsorption uptake (1.58 mg g^{-1}) compared to activated carbon (0.97 mg g^{-1}). This higher capacity was caused by the presence of hydroxylic, carboxylic, and polyphenolic groups. FTIR analysis before and after adsorption of boron suggested that the mechanism involved in the boron removal might be complexation." Sasaki et al. (2011) explains the study as follow: "Effective immobilization of boron in groundwater is a major challenge. Permeable reactive barrier (PRB) column tests for removal of borate have been investigated using MgO agglomerates as the primary

reactive material over 40 weeks. Additionally, saw dust was also blended with MgO agglomerates to facilitate for borate removal in this system. Boron accumulation was more than 1.6 times greater in the presence of saw dust, although MgO alone performed well. Increased boron accumulation in the presence of saw dust was primarily due to higher porosity of the PRB column, decreasing the impact of secondary $Mg(OH)_2$ passivating layers and leaving more reactive sites on MgO agglomerates. In addition, Mg^{2+} ions released from MgO agglomerates are complexed with carboxylic acids leached from saw dusts. This sequestration prevents the formation of bulky $Mg(OH)_2$ which is an ineffective sorbent for borate and covers the surfaces and passivating reactive sites on the MgO agglomerates. The morphologies of $Mg(OH)_2$ precipitated in the PRB column were also significantly affected by the presence of saw dust, with crystallization of needle-like particles of $Mg(OH)_2$ was prevented by Mg^{2+} ions–organic ligand complexation."

As mentioned in literature studies explained above and according to the results in this study, saw dust can be good candidate for boron removal from diluted boron waters according to presence of hydroxylic, carboxylic, and polyphenolic groups.

3.3. Chemical Precipitation and Adsorption with Espey Spring Water(b)

3.3.1. Chemical Precipitation with Espey Spring Water(b)

The results of chemical precipitation with 10 g of lime at 25 ºC temperature are shown in Table 22.

Table 22. *Results of chemical precipitation study performed with 10 g of lime at 25 ºC temperature*

Lime Amount [g]	B_2O_3 [g/L]	B_2O_3 [ppm]	B [g/L]	B [ppm]
10	0.957	957	0.297	297

The decrease from 3810 ppm to 297 ppm (92% removal efficiency) can be considered as a very good result in terms of chemical purification.

3.3.2. Adsorption with Espey Spring Water(b)

Adsorption results of Espey Spring Water(b) with 10 g of waste activated carbon (activated with 0.1 M NaOH) and with 10 g of pine cane (activated with 0.1 M NaOH), at 25 ºC are shown in Table 23.

Table 23. *Adsorption results of Espey Spring Water(b) using 10 g of Waste Activated Carbon (activated with 0.1 M NaOH) and using 10 g of Pine Cane (activated with 0.1 M NaOH)*

Adsorbent Type	B_2O_3 [g/L]	B_2O_3 [ppm]	B [g/L]	B [ppm]
Waste Activated Carbon	0.905	905	0.281	281
Pine Cane	0.853	853	0.265	265

It can be seen from these results that for waste activated carbon, the amount of boron remaining in the wastewater was 281 ppm. Considering that the initial boron concentration in water was 297 ppm, the boron

removal achieved was 16 ppm (5.4% removal efficiency) which was not sufficient. And also, for pane cane the amount of boron remaining in the wastewater was 265 ppm. Considering that the initial boron concentration in water was 297 ppm, the boron removal achieved was 32 ppm (10.8% removal efficiency) which was not sufficient removal result also.

However, when the percentage removal efficiencies were considered, it was seen that waste activated carbon and pine cane were not appropriate adsorbents for boron removal. This can be explained by the fact that the pore structure of the activated carbon was not suitable for boron adsorption or the lack of interaction between boron and the functional groups that might be present in the adsorbent.

Because of these inefficient results, it was decided to continue the study with the adsorbent almond shells since efficient and could be improved results were obtained in the second part of this study.

Adsorption Results of Espey Spring Water with different amounts of almond shell particles (Activated with HCl), at 25 ºC are shown in Table 24.

The results of adsorption experiments carried out using different amounts of adsorbent with an initial boron value of 297 ppm were as follows: for 2 g of adsorbent as a result of the experiment, boron removal was 130 ppm (43.8% removal efficiency); for 4 g of adsorbent, boron removal was 157 ppm (52.9% removal efficiency); for 8 g of adsorbent, boron removal was 163 ppm (54.9% removal efficiency); for 10 g of adsorbent boron removal was 163 ppm (54.9% removal efficiency); for 20 g of adsorbent, boron removal was 163 ppm (54.9% removal efficiency).

Table 24. *Adsorption results of Espey Spring Water using different amounts of almond shell particles (activated with hcl), at 25 ℃*

Amount of Adsorbent [g]	**B_2O_3 [g/L]**	**B_2O_3 [ppm]**	**B [g/L]**	**B [ppm]**
2	0.540	540	0.167	167
4	0.450	450	0.140	140
8	0.433	433	0.134	134
10	0.433	433	0.134	134
20	0.433	433	0.134	134

According to these results, as the amount of adsorbent increased, the removal efficiency increased up to a certain amount of adsorbent till 8 g of adsorbent. The reason for this could be explained by the increase in the available surface area and the increase in active sites in the increased surface area as the amount of adsorbent increased. At 8 g of adsorbent and later, the adsorption removal efficiency remained constant. The reason for this was thought to be that the adsorption event reached a dynamic equilibrium.

When literature data was examined about the effect of effect of adsorbent on adsorption, according to the data exists in the study of Giray (2010), Öztürk and Köse (2008), Çengeloğlu et al. (2007), Uslu (2010), Arıkan (2019), Öztürk and Kazak (2004) and Atalay Sönmez (2014), as the adsorbent amount increased, boron removal increased up to a level, then remained constant due to the dynamic equilibrium reached.

The studies were continued with 8 g, which was the amount of adsorbent that yielded the best result in the previous study.

The adsorption results of Espey Spring Water with 8 g of almond shell particles (Activated with HCl), at 25 ºC, at different pHs are shown in Table 25.

Table 25. *Adsorption results of Espey Spring Water using 8 g of almond shell particles (activated with HCl), at 25 ºC, at different pHs*

pH	B_2O_3 [g/L]	B_2O_3 [ppm]	B [g/L]	B [ppm]
4	0.554	554	0.170	170
7	0.450	450	0.140	140
10	0.346	346	0.107	107
11	0.398	398	0.124	124
12	0.467	467	0.145	145

The results of adsorption experiments carried out at different pHs with an initial boron value of 297 ppm were as follows: The boron removal at pH 4 was 127 ppm (42.8% removal efficiency), at pH 7 was 157 ppm (52.9% removal efficiency), at pH 10 was 190 ppm (64% removal efficiency), at pH 11 was 173 ppm (58.3% removal efficiency) and at pH 12 was 152 ppm (51.2% removal efficiency).

According these results, with an output value of 107 ppm (190 ppm removal, 64% boron removal efficiency), the optimum removal pH could be considered as pH 10. That was because of the reason explained in the discussion of the results given in Table 16.

When literature data was examined about the effect of pH on adsorption, optimum pH values for boron removal using different adsorbents are pH 7-9 with using modified perlite (Zincir, 2013); pH 7 with using cotton cellulose (Liu et al., 2007); pH 10 with using non-activated waste sepiolite (NAWS) and HCl-activated waste sepiolite (AWS) (Öztürk & Kavak, 2004); pH 7.5-8.5 with using vermiculite clay, pH 7.5-9 with using perlite (Baran, 2014); pH 10 with using granular iron hydroxide (GDH) (Atalay Sönmez, 2014); pH 8.2-8.5 with using aluminum based adsorbent (Irawan et al., 2011); pH 8-10 with using clay and modified clay (Karahan et al., 2006); pH 8-10 for all adsorbents as fly ash, zeolite, and demineralized lignite (Yüksel & Yürüm, 2009); pH 10 with using sepiolite (Öztük & Kavak, 2004); pH 5.13 with using natural pumpkin seed shell (Çelebi, 2020); pH 9 with using mineral adsorbents while pH 7 with using walnut shells and rice residues and pH 8 with using wheat residues **(**Jalali et al., 2016).

The studies were continued with 8 g of adsorbent and pH 10 which were the optimum values obtained.

The adsorption results of Espey Spring Water using 8 g of almond shell particles (activated with HCl), at 25 ºC, at pH 10, at different mixing speeds are shown in Table 26.

***Table 26**. Adsorption results of Espey Spring Water with 8 g of almond shell particles (Activated with HCl), at 25 ºC, at pH 10, at different mixing speeds*

Mixing Speed [rpm]	B_2O_3 [g/L]	B_2O_3 [ppm]	B [g/L]	B [ppm]
120	0.363	363	0.113	113
150	0.346	346	0.107	107
170	0.346	346	0.107	107
180	0.346	346	0.107	107
200	0.346	346	0.107	107

The results of adsorption experiments carried out at different mixing speeds with an initial boron value of 297 ppm were as follows: The boron removal at 120 rpm was 184 ppm (62% removal efficiency), at 150 rpm was 190 ppm (64% removal efficiency), at 170 rpm was 190 ppm (64% removal efficiency), at 180 rpm was 190 ppm (64% removal efficiency), and at 200 rpm was 190 ppm (64% removal efficiency).

According to these results, it was seen that the mixing speed had almost no significant effect on the adsorption efficiency. Only at 120 rpm, less efficiency was obtained compared to other and stable results. In summary, it could be said that the adsorption efficiency was independent of the mixing speed after 150 rpm.

These results very well confirm with the results reported in the literature for effect of mixing speed on adsorption for boron removal. For example, Korkmaz (2011) stated that using boron removal efficiency did not change with mixing speed in the study of boron removal using Purolite S 108 resin.

The studies were continued by using 4 g of adsorbent, at pH 10 and 150 rpm mixing speed at which the optimum values were obtained.

The adsorption results of Espey Spring Water with 8 g of almond shell particles (activated with HCl), at pH 10, at 150 rpm, at different temperatures are shown in Table 27.

The results of adsorption experiments carried out at different temperatures with an initial boron value of 297 ppm were as follows: The boron removal at 15 °C was 144 ppm (48.5%), at 25 °C was 190 ppm (64%), at 40 °C 122 ppm (41.1%), at 55 °C was 100 ppm (33.7%) and at 70 °C was 79 ppm (26.6%).

According to these results, the effect of temperature on adsorption efficiency was significant. As the temperature increased, the adsorption efficiency decreased. From these results, it was concluded that the

adsorption was exothermic which is a characteristics of physical adsorption. The temperature at which adsorption was most efficient was 25 °C.

Table 27*. Adsorption Results of Espey Spring Water using 8 g of almond shell particles (activated with HCl), at pH 10, at 150 rpm, at different temperatures*

Temperature [°C]	**B_2O_3 [g/L]**	**B_2O_3 [ppm]**	**B [g/L]**	**B [ppm]**
15	0.492	492	0.153	153
25	0.346	346	0.107	107
40	0.563	563	0.175	175
55	0.633	633	0.197	197
70	0.703	703	0.218	218

When literature data was examined about the effect of temperature on adsorption, Atalay Sönmez (2014) stated in her study as follows: "In the study conducted by Öztürk et al. (2005) on boron adsorption from water using batch and column experiments and fly ash, maximum boron removal occurred at temperature 25 ºC. Öztürk et al. (2008) investigated the effect of cerium oxide as an adsorbent material on boron removal from water using factorial experimental design method. Maximum boron removal occurred at temperature of 40 °C. In the study conducted by Kıpçak et al. (2012) on boron adsorption from aqueous solutions with waste calcined magnesite, the optimum temperature was 45 °C. In the study conducted by Kavak (2009), boron adsorption on calcined alunite was studied using a 23 factorial design. Boron removal decreased as temperature increased. The optimum optimum temperature was found to be 25 °C. In the study conducted by Polowczyk et al. (2013) using fly ash, it was found that boron adsorption increased with increasing temperature." Che Ku Mohd and İsmail (2020) stated that, maximum boron removal was obtained at 27°C with using the (MAZC) composite beads of mangrove bark, alginate and zeolite (MAZC) as an adsorbent. Thermodynamic studies have shown that this adsorption process was a spontaneous exothermic process.

Uslu (2010) stated as follows: "From the data obtained as a result of the experiments, it was observed that the adsorption behavior did not cause a significant change in the adsorption of boron by PVC-NMG in the temperature range examined (20-40 °C)." Kluczka et al. (2013) stated that using a new adsorbent natural clinoptilolite and amorphous zirconium dioxide (ZrO_2), the adsorption was exothermic. Bhagyaraj et al. (2021) stated as follows: "Haddabi et al. explored that for boron removal efficiency of date palm seed ash temperature on the adsorption process had a minor effect. Al-Ghouti et al. investigated the use of eggshell membrane (ESM) and modified eggshell membrane (MESM) as biosorbents for boron. The results indicated that the adsorption of boron preferentially occurred at 35 °C, which favor a spontaneous endothermic reaction."

The studies were continued with 8 g, pH 10, 150 rpm shaking speed and 25 °C which were the optimum values obtained.

The adsorption results of Espey Spring Water with 8 g of almond shell particles (Activated with HCl), at pH 10, at 150 rpm, at 25 °C, at different contact times are shown in Table 28.

Table 28. *Adsorption results of espey spring water using 8 g of almond shell particles (activated with HCl), at pH 10, at 25 °C, 150 rpm, at different contact times*

Contact time [h]	**B_2O_3 [g/L]**	**B_2O_3 [ppm]**	**B [g/L]**	**B [ppm]**
1	0.370	370	0.115	115
2	0.346	346	0.107	107
3	0.352	352	0.109	109
4	0.317	317	0.099	99
5	0.317	317	0.099	99

The results of adsorption experiments carried out as a function of time with an initial boron value of 297 ppm were as follows: The boron removal at 1 hour was 182 ppm (61.3%); at 2 hours was 190 ppm (64%); at 3 hours was 188 ppm (63%); at 4 hours was 198 ppm (66.7%); and at 5 hours was 198 ppm (66.7%).

When the adsorption results were evaluated, as the contact time increased, the adsorption efficiency increased from 1 hour to 4 hours. At the end of the 4 hours contact time, the system reached dynamic equilibrium.

When literature data was examined about the effect of contact time on adsorption;

Jalali et al. (2016) stated as follows: “B removal from aqueous solutions was investigated using natural easily available materials including bentonite, kaolinite, zeolite, waste calcite, and residues of wheat, rice and green shell of walnut as native and chemically modified with $FeCl_3$. The optimum time obtained for mineral sorbents and organic sorbents was 24 and 48 h, respectively.” Baran (2014) stated that optimum time values were 15 hours using vermiculite clay and 4 hours using perlite. In other studies; optimum contact times were found as 30 minutes using new adsorbent natural clinoptilolite and amorphous zirconium dioxide (ZrO_2) (Kluczka et al. 2013) and 24 hours with using the composite (MAZC) consisting of mangrove bark, alginate and zeolite as an adsorbent (Che Ku Mohd & İsmail, 2020). Atalay Sönmez (2014) stated in her study as follows: “According to the study conducted by Ferreira et al. (2006); boron removal from water was studied using Mg-Al and Mg-Fe hydrotalcite as adsorbent material. In the study, the time to reach equilibrium was found to be 120 minutes. In the study conducted by Wei et al. (2011); the design and production of environmentally friendly adsorbent materials for boron removal were studied. In the study, N-methyl glucamine, a natural biopolymer, and chitosan were functionalized by atom transfer radical polymerization and used as environmentally friendly adsorbent materials. Boron adsorption was 90% at the end of 8 hours of contact time. According to the study conducted by Ferreira et al. (2006); boron removal from water was studied using Mg-Al and Mg-Fe hydrotalcite as adsorbent material. In the study, the time to reach equilibrium was found to be 120 minutes. In the study conducted by Kıpçak et al. (2012) on boron adsorption from aqueous solutions with waste calcined

magnesite, the optimum contact time was determined as 420 minutes." Bhagyaraj et al. (2021) stated as follows: "Haddabi et al. explored that for boron removal efficiency of date palm seed ash contact time on the adsorption process had a minor effect." Saleh Al-dhawi et al. (2023) stated that with using CRB05 as the adsorbent optimum contact time reached was 255 minutes. Çelebi (2020) stated that with using pumpkin seed shell as adsorbent, optimum contact time reached was 5 minutes.

4. CONCLUSION

In the first part of this study, boron removal from wastewater taken from the Emet boric acid factory waste dam of Eti Mine Works was studied. Different adsorption studies were carried out in shaking water bath. Natural clays also zeolite which exit in the sites of Eti Mine Works and natural adsorbents as modified walnut shells, modified waste sunflower stems and modified waste corn cobs were used as adsorbents. Unfortunately, these adsorbents were found to be insufficient for the removal of boron from wastewater with high boron content as 5883 ppm.

An additional method was needed before adsorption. Since, the adsorption process with environmentally friendly adsorbents were insufficient for removing boron from industrial wastewater. It was thought that it would be more suitable to remove some boron from wastewater by chemical precipitation with lime then to continue to removal by adsorption using environmentally friendly adsorbents.

In the second part of this study, it was decided to study removal of boron from Espey Spring Water in the scope of social responsibility. The initial boron value of this water was 4590 ppm. After chemical precipitation with lime, the boron decrease from 4590 ppm to 424 ppm (as output value), 91% of removal, could be considered as a very good result in terms of purification. Afterwards, the adsorption process was started. 0.1 M HCl treated walnut shells, 0.1 M HCl treated almond shells and also 0.1 M NaOH treated sawdust were used separately as adsorbents. For walnut shells and almond shells, the effect of adsorbent amount, pH and particle size on adsorption were tried in the studies. And for saw dust, different dilution ratios were tried. Among the natural waste adsorbents used for boron removal of Espey Spring Water, the best results were obtained with 4 g of -63 μ almond shells at pH 9 with pure Emet Spring water with 23.5% removal efficiency and with 4 g of saw dust using 1/5 ratio diluted Espey Spring Water with 34.6% removal efficiency.

In the third part of this study, because of the fact that there wasn't not enough Espey Spring Water for further studies, spring water was provided from Emet, this time boron removal from 3810 ppm to 297 ppm (92% removal) was reached with two-stage chemical precipitation process. So, that was a good result again.

For adsorption studies, firstly modified waste activated carbon and modified pine cane were used as adsorbents. For waste activated carbon, boron removal achieved was 5.4% removal efficiency and for pine cane boron removal achieved was 10.8% removal efficiency. These were unfortunately inefficient results.

Since, improvable results were obtained with almond shells using not diluted but pure spring water in the second part of this study, studies were continued with almond shells used in part *2.2.2 Adsorption with Espey Spring Water(a).* To see the effect of these parameters on adsorption efficiency; the effect of the amount of adsorbent as 2, 4, 8, 10, 20 g; the effect of pH as 4, 7, 10, 11, 12; the effect of mixing speed as 120, 150, 170, 180, 200 rpm, the effect of temperature as 15 ℃, 25 ℃, 40 ℃, 55 ℃, 70 ℃ and effect of time as 1, 2, 3, 4, 5 hours were studied.

The best results were reached with using 8 g of adsorbent, at pH 10, at 150 rpm mixing speed, at 25 ºC and at 4 hours contact time. *For adsorbent amount effect*, best results were obtained with 8 g of adsorbent (54.9% removal efficiency); *for pH effect* (with 8 g of adsorbent, at 25 ºC), best results were obtained with pH 10 (64% removal efficiency); *for the effect of mixing speed effec*t (with 8 g of adsorbent, at 25 ºC, at pH 10), best results were obtained with pH 150 rpm (64% removal efficiency); *for the effect of temperature* (with 8 g of adsorbent, at pH 10, 150 rpm), best results were obtained with 25 ºC (64% removal efficiency), *for the of effect of contact time* (with 8 g of adsorbent, at pH 10, at 150 rpm, at 25 ºC), best results were obtained with 4 hours (66.7% removal efficiency). According to these results; as amount of adsorbent increased, boron removal increased. Since the surface area and active sites available for adsorption increased. Also, experimental results showed that the boron removal increased with the decreasing particle size. This implies that the adsorption may have the diffusion controlling mechanism. pH was found to be very important because of the fact that behaviour of boron in a solution highly depends on pH. Also, adsorption was found to be exothermic. And this is physical adsorption's characteristic property. As the shaking time increased, the interaction time of the adsorbent and adsorbed metals increased. So, the adsorption increased and reached equilibrium after a while.

With 66.7% removal efficiency, it was concluded that modified waste almond shell particles could be good candidate for boron removal from boron wasters having high boron content.

Compared to the results in the second part of this study (23.5% removal efficiency) more efficient results were obtained with 66,7% removal efficiency with almond shells for boron removal. The reason for this was in the second part of this study, initial boron after single chemical precipitation boron value of Espey Spring Water was 424 ppm. However, in the third part of this study, initial boron after two-stage chemical precipitation boron value of Espey Spring Water was 297 ppm. As explained in literature part, 1.2 Boron Chemistry*," if the total boron concentration in the aqueous solution is less than 270 mgB/L, it is known that only* H_3BO_3 *and* $B(OH)_4^-$ *ions are present in the environment. Conversion to polyborates occurs between pH 6-11 and at higher concentrations (>0.025 M).*" So, in the second part of this study boron value of spring water was 424 ppm before adsorption and at this boron value, polyborates might occurred since boron concentration was higher than 270 ppm and initial pH was 11.67 (after chemical precipitation). However, in the third part of this study, boron concentration of spring water was 297 ppm and initial pH was 11.34 (after chemical precipitation). And at this 297 ppm, it was thought that mainly H_3BO_3 and $B(OH)_4^-$ ions existed in the water compared to polyborates which was thought to be as newly started to occur. Because of this reason and also with the effect

of the optimum parameters applied such as adsorbent amount, pH, mixing speed, temperature and contact time, more efficient results were obtained compared to the second part of this study consisting adsorption with almond shells.

In further studies, it is recommended to determine which adsorption model the results fit into and also to determine thermodynamic parameters and the kinetic model which the adsorption fits into.

In summary, in the studies in the literature, in general, synthetically prepared boron solutions were studied for boron removal. From environmental and economic perspective and in the scope of social responsibility; evaluating natural waste adsorbents, as almond shells for boron removal from spring waters which have high boron content in the adsorption process, makes this study specific.

For further studies, it is hoped that unlike the methods used in Eti Mine Works, adsorption which is a useful, easy and economic method, will also ensure that the boron concentration in boron waters will be lowered below the regulation limit values in Turkey.

AUTHOR CONTRIBUTIONS

Methodology, İ.Ç.G and İ.A.; laboratory work, İ.Ç.G.; manuscript-original draft, İ.Ç.G.; manuscript-review and editing, İ.Ç.G and İ.A. All authors have read and legally accepted the final version of the article published in the journal.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

REFERENCES

Anonim (2010). TC Çevre ve Şehircilik Bakanlığı, Su Kirliliği Kontrolü Yönetmeliği, Dec.31, Resmi Gazete, 25687, 2010. https://webdosya.csb.gov.tr/db/cygm/icerikler/skky-2018-20180226120233.docx

Arıkan, T. (2019). Sulu Çözeltideki Bor İyonlarının Sepiyolit İle Giderimi. *KSÜ Tarım ve Doğa Dergisi, 22*(2), 333-338**.** https://doi.org/10.18016/ksutarimdoga.v22i42694.498284

Akkurt, F., Yörükoğlu, A., Aktosun, Z., & Yargıçoğlu, P. (2022). Reducing the Amount of Boron in the Wastewater of a Boron Processing Plant by Chemical Precipitation. *Iranian Journal of Chemistry and Chemical Engineering*, *41*(10), 3400-3406. https://doi.org/10.30492/ijcce.2022.529108.4698

Aslan, K. (2020) *Borik Asitin Derişik Sulu Çözeltilerinden Modifiye Aktif Karbon ve Aljinat Bazlı Adsorbanlar ile Giderilmesi*, MSc Thesis, Süleyman Demirel University.

Atalay Sönmez, N. (2014) *Sulardan Adsorpsiyon Yöntemi İle Bor Giderimi*, MSc Thesis, Pamukkale University.

Ateş, Ç. (2018) *Ardışık Kimyasal ve Elektrokimyasal Arıtma ile Bor İçerikli Atık Sudan Bor Giderimi*. MSc Thesis, Ankara University.

Bara, M. A., & Abba, M. U. (2025). Boron removal from industrial wastewater using hybrid adsorption-membrane system. *International Journal of Agricultural and Veterinary Science*, *7*(1). https://doi.org/10.70382/mejavs.v7i1.030

Baran, P. (2014) *Atık Sulardan Bor Gideriminde Modifiye Doğal Kil Minerallerinin Kullanılabilirliğinin Araştırılması*. PhD Thesis, İTÜ.

Bhagyaraj, S., Al-Ghouti, M. A., Kasak, P., & Krupa, I. (2021). An updated review on boron removal from water through adsorption processes. *emergent mater. (4),* 1167–1186. https://doi.org/10.1007/s42247-021-00197-3

Bilen, M., Ateş, Ç., & Bayraktar, B. (2018). Yanıt yüzey yöntemi ile bir bor fabrikası atık suyu kimyasal arıtma sürecinde optimum koşulların belirlenmesi. *Gazi Üniversitesi Mühendislik Mimarlık Fakültesi Dergisi, 33*(1). https://doi.org/10.17341/gazimmfd.406798

Bilici Başkan, M., & Atalay, N. (2014). Boron contamination in drinking - irrigation water and boron removal methods. *Pamukkale Univ Muh Bilim Derg*, *20*(3), 78-84. https://doi.org/10.5505/pajes.2014.47955

Çelebi, H. (2020). Doğal Kabak Çekirdeği Kabuğunun Bor Adsorpsiyon Kapasitesi, *Bitlis Eren Üniversitesi Fen Bilimleri Dergisi*, *9*(4), 1698–1710. https://doi.org/10.17798/bitlisfen.667331

Çelebi Gürsoy, İ., & AR, İ. (2024). *Removal of Boron and Boron Compounds From Waste Waters.* In*:* International Conference on Advanced Materials Science & Engineering and High Tech Devices Applications Oct. 24-26 2024, Ankara, Türkiye.

Che Ku Mohd, C. K. N. A., & Ismail, M. H. S. (2020). Optimization of boron removal from aqueous solutıon via adsorptıon using composite beads of mangrove bark, alginate and zeolite. *Journal of Chemical Engineering and Industrial Biotechnology*, *3*(1), 1-12. https://doi.org/10.15282/jceib.v3i1.3739

Çengeloglu, Y., Tor, A., Arslan, G., Ersoz, M., Gezgin, S. (2007). Removal of boron from aqueous solution by using neutralized red mud, *Journal of Hazardous Materials, 142*(1-2), 412–417. https://doi.org/10.1016/j.jhazmat.2006.08.037

Doğan, G., Sabah, E., & Erkal, T. (2005, 9-12 June). *Borun Çevresel Etkileri Üzerine Türkiye'de Yapılan Bilimsel Araştırmalar.* In: Türkiye International Mining Congress, İzmir

Eti Mine Works Quality Management System. *B_2O_3 Analyse Book.*

Fadaei, Abdolmajid (2022). A Comparison of Techniques of Boron Removal from Water and Wastewater. *Journal of Environmental Science and Sustainable Development, 5*(2), 404-435. https://doi.org/10.7454/jessd.v5i2.1151

Giray, G. (2010). *Sülfonamid Esaslı N-Metil-D-Glukamin Fonksiyonlu Polimerik Sorbentle Çözeltilerden Bor Giderimi*, MSc Thesis, İTÜ, İstanbul.

Jaouadi, M. (2021). Characterization of activated carbon, wood sawdust and their application for boron adsorption from water. *International Wood Products Journal, 12*(1), 22–33. https://doi.org/10.1080/20426445.2020.1785605

Jalali, M., Rajabi, F.H., & Ranjbar, F. (2016). The removal of boron from aqueous solutions using natural and chemically modified sorbents. *Desalination and Water Treatment, 57*, 8278-8288. https://doi.org/10.1080/19443994.2015.1020509

Karahan, S., Yurdakoç, M., Seki, Y., & Yurdakoç, K. (2006). Removal of boron from aqueous solution by clays and modified clays. *Journal of Colloid and Interface Science*, *293*(1), 36-42. https://doi.org/10.1016/j.jcis.2005.06.048

Keren, R., & Mezuman, U. (1981). Boron Adsorption by Clay Minerals Using a Phenomenological Equation. *Clays and Clay Minerals, 29*(3), 198-204. https://doi.org/10.1346/ccmn.1981.0290305

Kluczka, J., Korolewicz, T., Zołotajkin, M., Simka, W., & Raczek, M. (2013). A new adsorbent for boron removal from aqueous solutions. *Environmental technology*, *34*(9-12), 1369–1376. https://doi.org/10.1080/09593330.2012.750380

Korkmaz, M. (2011) *Bor İçeren Sulardan Purolite S 108 Reçinesi Kullanarak Bor Giderimi*. MSc Thesis, Balıkesir Üniversitesi.

Kökkılıç, O. (2003) *Kırka Bor İşletmesi Atık Göletlerindeki Sulardan Borun Kazanılması*. MSc Thesis, İTÜ.

Liao, L., Chen, H., He, C., Dodbiba, G., & Fujita, T. (2024). Boron Removal in Aqueous Solutions Using Adsorption with Sugarcane Bagasse Biochar and Ammonia Nanobubbles. *Materials, 17*(19), 4895. https://doi.org/10.3390/ma17194895

Liu, R., Ma, W., Wang, L. (2007). Effect of pH on biosorption of boron onto cotton cellulose. *Desalination, 207*, 257–267. https://doi.org/10.1016/j.desal.2006.07.012

Liu, H., Qing, B., Ye, X., Li, Q., Lee, K., & Wu, Z. (2009). Boron adsorption by composite magnetic particles. *Chemical Engineering Journal, 151*(1-3), 235-240. https://doi.org/10.1016/j.cej.2009.03.001

Liu, X., Xu, C., Chen, P., Li, K., Zhou, Q., Ye, M., Zhang, L., & Lu, Y. (2022). Advances in Technologies for Boron Removal from Water: A Comprehensive Review. *International Journal of Environmental Research and Public Health*, *19*(17), 10671. https://doi.org/10.3390/ijerph191710671

Öcal, Z. B., Öncel, M. S., Keskinler, B., Khataee, A., & Karagündüz, A. (2024). Sustainable treatment of boron industry wastewater with precipitation-adsorption hybrid process and recovery of boron species. *Process Safety and Environmental Protection*, *182*, 719-726. https://doi.org/10.1016/j.psep.2023.12.006

Öztürk, N., & Kavak, D. (2004). *Adsorption of Boron from Aqueous Solutions by Sepiolite using Full Factorial Design: I. Batch Studies.* In: 2nd International Boron Symposium, Eskişehir, Türkiye.

Öztürk, N., Köse T. E. (2008). Boron removal from aqueous solutions by ion exchange resin: Batch studies, *Desalination, 227*(1-3), 233–240. https://doi.org/10.1016/j.desal.2007.06.028

Rodarte, D., Smith, R.S. (2014). A Comparison of Methods for Boron Removal From Flowback and Produced Waters. https://jpt.spe.org/comparison-methods-boron-removal-flowback-and-produced-waters

Saleh Al-dhawi, B. N., Mohammad Kutty, S. R., Baloo, L., Mohammed Yahya Almahbashi, N., Mohsen Alawag, A., Saeed Ghaleb, A.A., Hussaini Jagaba, A., Abdulrahman Al-Mekhlafi, A. (2023). Boron removal from produce water through adsorption. *BIO Web of Conferences, 73*, 02002. https://doi.org/10.1051/bioconf/20237302002

Selimoğlu, V., & Boncukcuoğlu, R. (2019). Bor Çözeltilerinden Kimyasal Çöktürmeyle Bor Giderimi. *Journal of the Institute of Science and Technology, 9*(3), 1343-1350. https://doi.org/10.21597/jist.515526

Sütçü, L. (2005) *Removal of Boron From Waters Using Fly Ash*. MSc Thesis, Graduate School of Engineering and Science of İzmir Institute of Technology.

Seyhan, S., Seki, Y., Yurdakoç, M., & Merdivan, M. (2007). Application of iron-rich natural clays in Çamlica, Turkey for boron sorption from water and its determination byfluorimetric-azomethine-H method. *Journal of Hazardous Materials, 146*(1-2), 180–185. https://doi.org/10.1016/j.jhazmat.2006.12.008

Uslu, A. S. (2010) F*onksiyonel Hale Getirilmiş Pvc Esaslı Adsorban İle Sulu Çözeltilerden Bor Giderimi*, MSc Thesis, İTÜ.

Ünlü, M. İ., Bilen, M., & Gürü, M. (2013). Kütahya-Emet Bölgesi Yeralti Sularinda Bor Ve Arsenik Kirliliğinin Araştırılmasi. *Gazi Üniversitesi Mühendislik Mimarlık Fakültesi Dergisi*, 26(4).

Yağmur, Y. (2012) *Birlikte Çöktürme-Mineralizasyon Yöntemi ile Sulu Çözeltilerden Bor Kazanımı*, MSc Thesis, İTÜ.

Yiğitbaşıoğlu, H. (2004). Türkiye İçin Önemli Bir Maden: Bor. *Coğrafi Bilimler Dergisi, 2*(2), 13-25. https://doi.org/10.1501/Cogbil_0000000046

Yüksel, S., & Yürüm, Y. (2009). Removal of Boron from Aqueous Solutions by Adsorption Using Fly Ash, Zeolite, and Demineralized Lignite. *Separation Science and Technology, 45*(1):105-115. https://doi.org/10.1080/01496390903256042

Zeytuncu, B., Pasaoglu, M. E., Eryildiz, B., Kazak, A., Yuksekdag, A., Korkut, S., Kaya, R., Turken, T., Ceylan, M., & Koyuncu, I. (2023). Application of different treatment systems for boron removal from industrial wastewater with extremely high boron content. *Journal of Water Process Engineering, 55*(104083). https://doi.org/10.1016/j.jwpe.2023.104083

Zincir, E. (2013) *Modifiye Edilmiş Perlit ile Atık Sulardan Bor Giderimi*, MSc Thesis, İTÜ.