

# Boron removal from aqueous solutions by activated carbon impregnated with salicylic acid

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## Abstract

In this study, the removal of boric acid from aqueous solution by activated carbon impregnated with salicylic acid was studied in batch system. pH, adsorbent amount, initial boron concentration, temperature, shaking rate and salicylic acid film thickness were chosen as parameters. Boron removal efficiencies increased with increasing adsorbent amount, temperature and pH, decreasing initial boron concentration. As thickness of salicylic acid film on activated carbon becomes thin up to 0.088 nm, the efficiency increased, and then, the efficiency decreased with becoming thinner than 0.088 nm of salicylic acid film. Shaking rate was no effect on removal efficiency. In result, it was determined that the use of salicylic acid as an impregnant for activated carbon led to the increase of the amount of boron adsorbed. A lactone ring, being the most appropriate conformation, forms between boric acid and –COOH and –OH groups of salicylic acid.

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**Keywords:** Activated carbon; Adsorption; Boron; Impregnation; Salicylic acid

## 1. Introduction

Boron is one of the most important underground riches of Turkey having 72% of the World reserves. Colemanite, ulexite and tincal are the most mined ores. After these ores is mined, they are concentrated. A half of concentrated colemanite and tincal is processed in plants in Bandırma, Turkey and their remainder and all the ulexite are exported to various countries. Thousands of tons of solid and liquid wastes form in both concentration plants and the plants which boron compounds are produced. Boron from these wastes to environment brings about various pollutions in the land, the underground water and the surface water. The waters contained with more than a certain concentration of boron have negative effects on plants, animals and human beings.

Many researches have been carried out to remove boron emitted from both boron industries and industries using boron compounds. In one of these studies, boron has been removed by ion exchange method using an anionic ion exchanger, sold

by trade name WOFATITE MK 51 in alkaline medium [1]. In another study, boron removal from geothermal waters has been carried out using ion exchange method at 4–5 pH and 90–95 °C [2]. Also, Hanay et al. [3] studied the parameters affecting the boron removal from thermal waters by ion exchange method and developed a mathematical model showing which boron removal fitted pseudo-second order kinetics. Boncukçuoğlu et al. [4] investigated boron removal from boron containing waters prepared synthetically, using Amberlite IRA 743 boron specific resine and improved a mathematical model and Yılmaz et al. [5] studied boron removal from water containing boron in a continuous reactor and obtained 99% removal under optimum conditions by using Amberlite IRA 743 boron specific resine.

Reactions between boric acid and borates with 1,3-diols have been studied by various researchers. Ristic and Rajakovic [6] have investigated boric acid extraction from aqueous solution by the solutions of 1,3-diols in an organic solvent. Kahraman [7] has removed boron from aqueous solutions using some 1,3-diols in the presence of sodium, calcium, magnesium and chloride ions. Peterson [8] has examined in detail boron extraction by using various derivatives of salicylic acid (3,5-ditertiary dodecyl salicylic acid, 5-tertiary amyl salicylic acid, 3,5-ditertiary dodecyl salicylic acid). In addition, new aliphatic 1,3-diols have been syn-

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### Nomenclature

$A$	the surface area of SA film on ACISA ( $\text{m}^2/\text{g}$ )
AC	powdered activated carbon
ACISA	activated carbon impregnated with salicylic acid
$B$	amount of SA on ACISA ( $\text{g}/\text{g}$ )
$C$	boron concentration in the solution after adsorption ( $\text{mg}/\text{L}$ )
$C_0$	initial boron concentration in the solution ( $\text{mg}/\text{L}$ )
$E_a$	activation energy ( $\text{kcal mol}^{-1}$ )
$K_c$	adsorption equilibrium constant
$q_e$	amount of boron adsorbed at equilibrium ( $\text{mg}/\text{g}$ )
$q_t$	the amount of boron adsorbed at $t$ time ( $\text{mg}/\text{g}$ )
SA	salicylic acid
$t$	time (min)
$T$	temperature ( $^{\circ}\text{C}$ , K)

### Greek symbol

$\rho$	density of salicylic acid ( $1443 \times 10^6 \text{ g}/\text{m}^3$ )
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thesized to use in the solvent extraction of boric acid. In one of these investigations, 1.1–2.0 M boric acid solutions which pH is adjusted to 2 have been extracted by 1,3-diols and the best yield has been taken by benzylic substituted 1,3-butanol [9]. In another study, boron removal has been investigated by the reactants containing various functional groups and the extractants have been classified [10]. Both activated carbon and activated carbon impregnated with various compounds have been used in boric acid and borax removal from wastewaters. In a study on this topic, boric acid and borax sorption have been investigated by using activated carbon impregnated citric and tartaric acid [11]. Öztürk and Kavak [12] improving a model on boron removal by adsorption from aqueous solutions by using activated carbon have found out that pH and temperature of the solution are effective on boron removal. Peak et al. [13] have examined adsorption mechanisms of boric acid and borax on hydroferric oxide by using ATR-FTR spectroscopic measurement techniques and determined that boric acid is adsorbed on hydroferric oxide by both physical adsorption and bond changing reactions. Keren and Sparsk [14] have used pyrophyllite for boron removal and found that boron adsorption increases by increasing of ionic strength, and also, boron adsorption capacity of pyrophyllite is more than that of montmorillonite. In another study, Yılmaz et al. [15] examined boron removal from water whose boron range was 100–1000 mg/L in an electrochemical reactor and accomplished to remove 97% of boron content. In a study by Öztürk and Kavak, fly ash as an adsorbent was used for boron removal from aqueous solution. The authors observed that the adsorption data conformed to the second-degree kinetics model and also, in the isotherm studies, experimental data fitted to Langmuir isotherm model [16]. In another study, the same researchers investigated boron removal from aqueous solution by adsorption on sepiolite waste and activated sepiolite waste and applied Yoon–Nelson models to the experimental data in order to predict the breakthrough curves and to determine the

characteristic parameters of the column useful for process design [17].

In the present study, being based on the reaction between salicylic acid and boric acid or borate ion, it was examined the parameters affecting boron adsorption on activated carbon impregnated with salicylic acid (ACISA).

## 2. Materials and methods

For the runs, 5–50 ppm boron solutions were prepared synthetically, mixing boric acid ( $\text{H}_3\text{BO}_3$ ) and disodium tetraborate decahydrate ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) solutions with equal concentrations in various ratios. Due to undissolving salicylic acid (SA) in aqueous solution, it was impregnated on activated carbon (AC) and so, a large surface area was obtained for SA forming a thin layer on AC having a large surface area. Activated carbon impregnated with salicylic acid (ACISA) produced in this way was used as an adsorbent in adsorption of boric acid and/or borate ion. AC supplied from J.T. Baker and other chemicals from Acros. AC has an apparent density of  $150 \text{ kg}/\text{m}^3$ , surface area of  $609 \text{ m}^2/\text{g}$  and particle size of  $-125 \mu\text{m}$  and specific pore volume of  $0.4543 \text{ cm}^3/\text{g}$ .

Both impregnating experiments were carried out in a 250 ml-erlenmeyer shaken by a shaker marked Julabo. In impregnating experiments, a gravimetric analysis was designated to find saturation value by SA of AC. For this purpose, after 2000 g SA was dissolved in 100 ml of diethyl ether, 10 g AC was added to this solution and the mixture was shaken for 24 h. Then, 25 ml of clear part of erlenmeyer content was taken to a 50 ml-beherglass, diethyl ether content was evaporated and amount of obtained SA was found by weighting. Amount of SA impregnated on AC was found by subtracting amount of SA in diethylether phase after impregnating from amount of SA in diethylether phase at the starting. In result, it was determined that 1 g of activated carbon kept 0.0895 g of salicylic acid.

In addition, to make SA layer on AC thin, 12 g of ACISA (amount containing about 1 g SA) was shaken in 100, 200, 300, 400, 500, 600, 800 and 1000 ml of diethyl ether, respectively, for 24 h. The amounts of SA passing to diethyl ether phase were found gravimetrically by evaporating diethyl ether and weighting residue SA. Later, amounts of SA in ACISA samples thinned were determined by subtracting SA amounts passing diethylether phase from amount of SA in ACISA prepared at the initial. And then, these samples were used to investigate the effect of thickness of salicylic acid layer (nm) or SA amount on ACISA (g/g) on boron removal.

Surface areas of both AC and ACISA were measured by Quantochrome QS-17 model BET apparatus and SA thickness on ACISA was calculated from its mass as follows:

$$\text{thickness of SA on AC (nm)} = \frac{B}{A\rho} \times 10^9 \quad (1)$$

where  $A$  is the surface area of SA film on ACISA ( $\text{m}^2/\text{g}$  ACISA),  $B$  the amount of SA on ACISA ( $\text{g SA}/\text{g ACISA}$ ) and  $\rho$  is density of salicylic acid ( $1.443 \times 10^6 \text{ g}/\text{m}^3$ ), respectively.

Properties of ACISA used in boron removal experiments are given in Table 1. In adsorption studies, temperature, pH, shaking

Table 1  
Properties of activated carbon impregnated with salicylic acid (ACISA)

Adsorbent	Surface area of ACISA (m <sup>2</sup> /g) (A)	SA amount on ACISA (g/g) (B)	SA thickness on ACISA (nm) (B/Aρ)
ACISA	559	0.0895	0.111
ACISA stirred in 100 ml-diethylether	569	0.0798	0.097
ACISA stirred in 200 ml-diethylether	579	0.0783	0.096
ACISA stirred in 300 ml-diethylether	583	0.0750	0.089
ACISA stirred in 400 ml-diethylether	585	0.0740	0.088
ACISA stirred in 500 ml-diethylether	588	0.0728	0.086
ACISA stirred in 600 ml-diethylether	590	0.0702	0.082
ACISA stirred in 800 ml-diethylether	596	0.0680	0.079
ACISA stirred in 1000 ml	601	0.0653	0.075
AC	609	0.0000	0.000

Table 2  
Experimental parameters used for boron removal and their values

Parameters	Chosen parameter values
Boron concentration (ppm)	5, 10, 25, 50
Adsorbent (ACISA) amount (g/L)	5, 10, 20, 40
Temperature (°C)	25, 30, 40, 50
Shaking rate (rpm)	150, 175, 200, 225
pH	4.68, 7.45, 7.92, 8.08

rate, initial boron concentration, adsorbent (ACISA) amount and the surface area of ACISA were used as parameters whose values are given in Table 2.

Adsorption experiments have been carried out in 250 mL-erlenmayer flask shaken using a shaker marked Julabo. Brims of erlenmayer flasks were covered to prevent evaporation of the solutions. In the experiments which ACISA was used as an adsorbent, 100 mL-boron solutions having definite concentrations and pH were put in a series of 250-mL erlenmayer flasks in shaker adjusted to a determined temperature and a definite amount of ACISA was added to these solutions. After each of the mixtures was shaken in various periods, they were filtered by blue band filter paper (Schleicher Schuell). In addition these, also, experiments with AC unimpregnated with SA have been carried out under conditions which boron concentration was 25 ppm, solid to liquid ratio 2 g AC/100 mL solution, temperature 30 °C, pH 4.68 and shaking rate 175 rpm.

Boron analysis in the solution were carried out by Carmin method using a spectrophotometer, 8500 II Biochrom marked, at 585 nm wave length and obtained results were used in

calculation of boron removal, as follows:

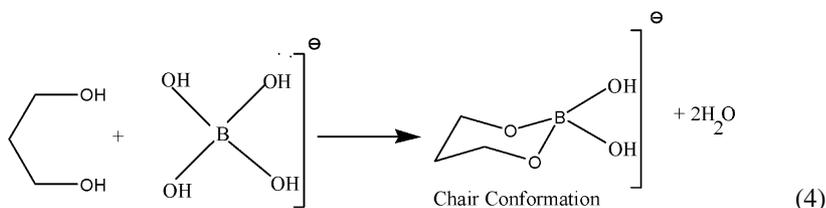
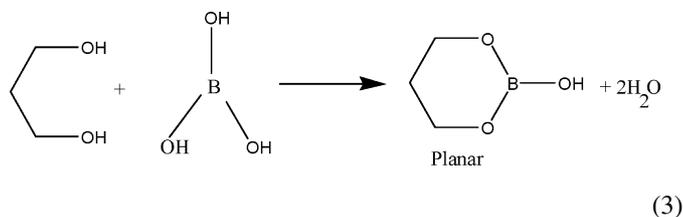
$$\text{boron removal} = \frac{C_0 - C}{C_0} \quad (2)$$

where  $C_0$  and  $C$  are boron concentrations in solution before and after adsorption, respectively. Both the impregnation and adsorption experiments and boron analysis were repeated three times at least and their arithmetical averages were used as result.

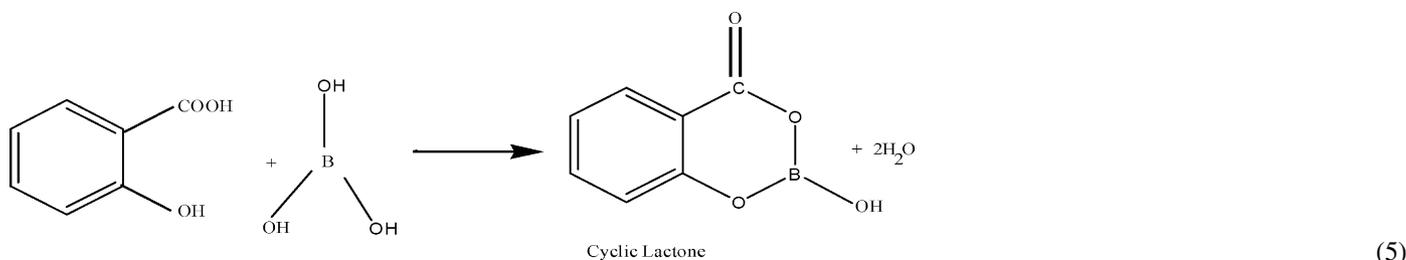
### 3. Results and discussion

#### 3.1. Reactions

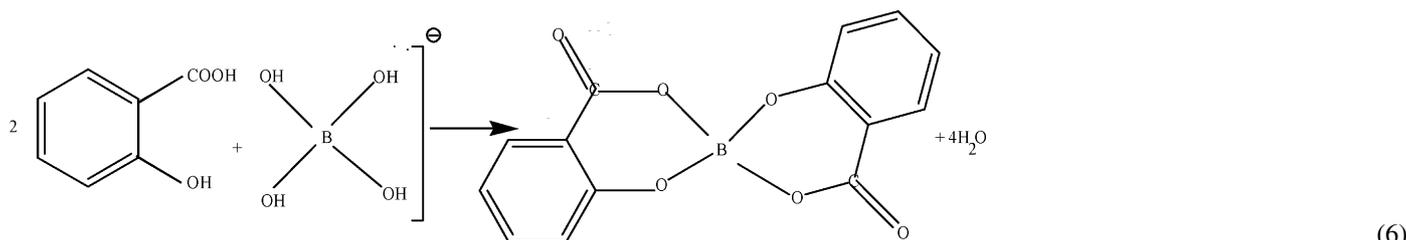
*Cis*-1,3-diols rapidly and reversibly form the ring structures with boric acid and borate in aqueous solution. These structures are an unstrained planar six-membered ring with trigonal boric acid and a nonplanar ring in puckered chair form with the tetrahedral borate anion. The formation of anionic complexes have been confirmed by Raman, C<sup>13</sup> and B<sup>11</sup> spectroscopy [18,19]. Further, Oertel's Raman datas have given direct evidence for chair conformation for 1,3-diol-borate complex [20]. Van Duin et al [21] have established a "charge rule" for determining pH stability of the different complexes. According to this rule, neutral complexes with diols form at lower pH than  $pK_a$  of boric acid and anionic complexes at higher pH than  $pK_a$  of boric acid. The reactions of boric acid and borate anion with *cis*-1,3-diols are given as follows [22,23].



The reactions of boric acid and borate anion with salicylic acid also may be stated similarly.



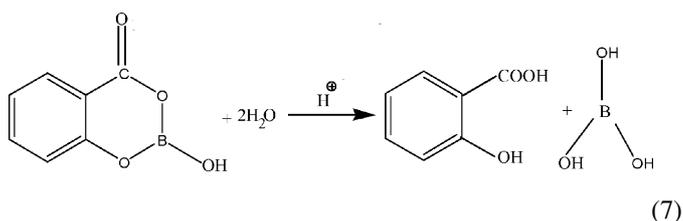
(5)



(6)

Because pH of solution ( $\leq 8.08$ ) is smaller than  $pK_a$  ( $pK_a = 9.23$ ) of boric acid and aromatic ring in salicylic acid structure is present, it was thought that occurring product must be planar. The presence of this product has been shown in a paper [24].

Here, lactone structure forming between SA and boric acid has been verified by literature, and also, X-ray data have been submitted in some papers [25,26]. It is one of well-known reactions of organic chemistry that the forming lactone can be easily hydrolyzed with water to compounds occurring it, as seen the following.



(7)

So boric acid can be obtained as pure and ACISA can be reused by gaining. In according to above mechanism, it may be thought that AC catches SA and adsorbs it in the most suitable position or conformation. It is accepted that the first stage which SA is adsorbed on AC is a physical adsorption. Here, AC surface with macro- and micro-pores and channels has been covered by multilayer of SA. When it was made this film layer thin by diethylether, it was seen that better boron removal had been ensured by obtained adsorbent. Because, the most appropriate conformation to increase boron removal is so that aromatic ring, being hydrophob end is inside end  $-COOH$  and  $-OH$  functional groups, being hydrophyl ends being outside and so that hydrophyl ends may catch boric acid easily. In this case, sterical effects are minimum and efficiency increase is inevitable. In experiments carried out with both ACISA and ACISA made SA layer thin with various amounts of diethylether, boron removal results verify these approaches.

### 3.2. The effect of pH

In order to investigate the effect of pH on boron removal, the experiments were carried out at various pHs, in which solid to liquid ratio was taken 20 g/L, initial boron concentration 25 ppm, shaking rate 175 rpm and temperature 30 °C. The solutions with different pH were prepared by mixing boric acid solution containing 25 ppm boron and borax solution containing 25 ppm boron at various ratios. Obtained data are given graphically in Fig. 1. In these experiments, pHs of boric acid and borax solutions containing each 25 ppm B were 4.68 and 8.08, respectively. Another boron solutions were prepared by mixing these solutions in various ratios and their pHs changed between 7.45 and 7.92. Boron removal increased with increasing pH of solution as seen in Fig. 1. It was thought that the increase of pH may cause to the neutralization reaction between SA on AC and  $OH^-$  ions in aqueous solution, a small part of SA on AC may pass to the aqueous solution, and channels and porosities on ACISA may be opened. This situation leads to more boron removal. Besides, according to literature, dimerical complex in Eq. (6) must occur in this pH level [22,27]. It was thought that the dimerical com-

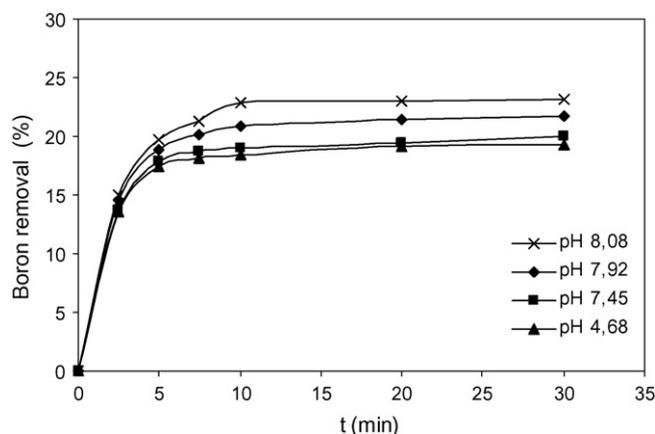


Fig. 1. The effect of initial pH on boron removal.

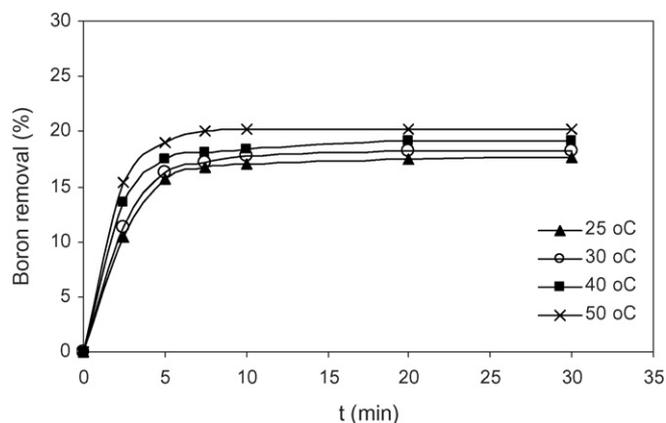


Fig. 2. Effect of temperature on boron removal.

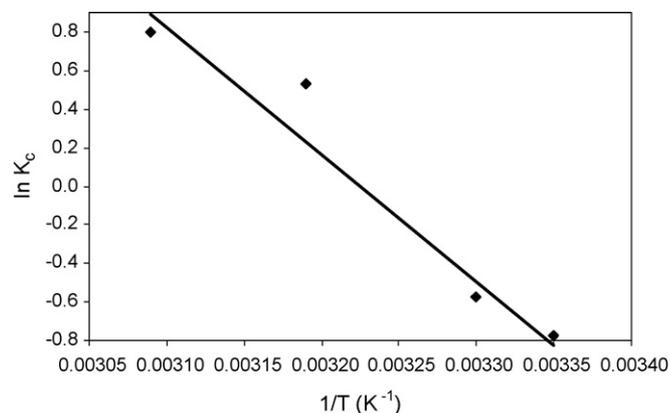


Fig. 4. Arrhenius graph.

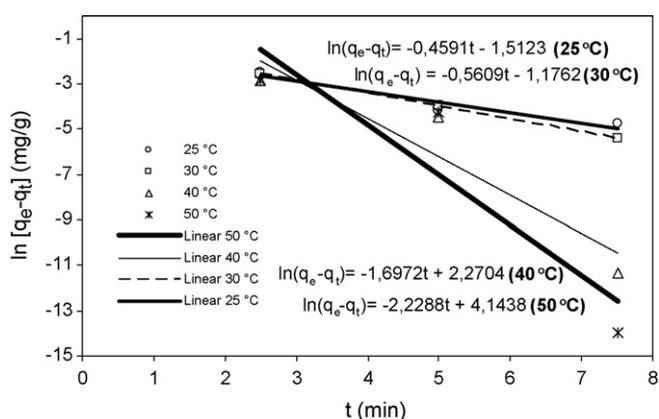


Fig. 3. Lagergreen graph for temperature.

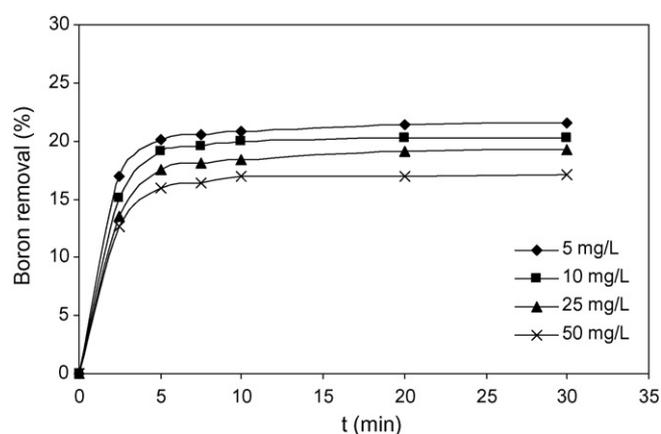
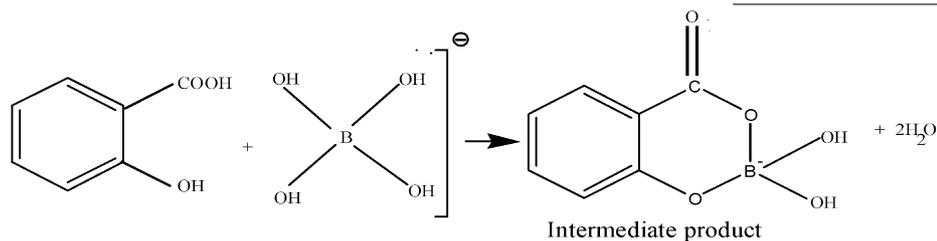


Fig. 5. The effect of initial boron concentration on boron removal.

plex formed in two stages, in the first stage, by the following reaction, an ionic complex formed between 1 mol SA on ACISA and 1 mol borate ion and in the second stage, the complex ion passing to solution reacted with a second molecule of SA on ACISA for the purpose of dimeric complex bonding to ACISA



(8)

### 3.3. The effect of temperature

In order to investigate the effect of temperature on boron removal the experiments were done at 25, 30, 40 and 50 °C. In the experiments which solid-to-liquid ratio was taken 20 g/L, initial boron concentration 25 ppm, shaking rate 175 rpm and pH 4.68, the efficiency increased with increasing temperature and the biggest efficiency was obtained at 50 °C as seen in Fig. 2.

On the other hand, the temperature data were applied to Lagergreen model and  $\ln(q_e - q_t)$  versus  $t$  was plotted by using experimental data obtained at various temperatures (Fig. 3) and

then, graph of  $\ln K_c$  from this graph versus  $1/T$ , called Arrhenius graph (Fig. 4), showed that activation energy of this process was  $54.85 \text{ kJmol}^{-1}$ . So, it was determined that because it was bigger than  $41.8 \text{ kJmol}^{-1}$ , the process was a chemisorption process [28] and boron removal should increase with increase in temperature.

### 3.4. The effect of initial boron concentration

In determining the effect of initial boron concentration on boron removal, it was used the solutions containing 5, 10, 25 and 50 mg/L-boron and reached adsorption equilibrium in 10 min. In the experiments which solid-to-liquid ratio was kept constant at 20 g/L, shaking rate at 175 rpm, pH at 4.68 and temperature at 30 °C, adsorption efficiency lowered with increasing initial boron concentration, but adsorbed boron amount per amount of adsorbent increased, as seen in Figs. 5 and 6.

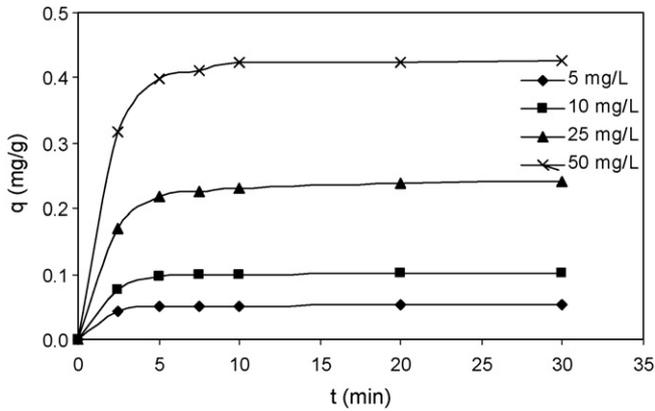


Fig. 6. The effect of initial boron concentration on boron removal per unit adsorbent.

3.5. The effect of adsorbent amount

The effect of adsorbent amount on boron removal was investigated in 5, 10, 20 and 40 g/L solid-to-liquid. In these experiments, initial boron concentration was kept constant at 25 ppm, shaking rate at 175 rpm, pH at 4.68 and temperature at 30 °C. As seen in Fig. 7, adsorption efficiency increased with increased adsorbent amount and adsorption equilibrium established in first 10 min.

3.6. The effect of shaking rate

The effect of shaking rate on boron removal was examined at shaking rates of 150, 175, 200 and 225 rpm. In these experiments, adsorbent dose was kept constant at 20 g/L, initial boron concentration at 25 ppm, pH at 4.68 and temperature at 30 °C. The obtained data showed that shaking rate was not effect on boron removal. This case stated fact that a chemical reaction took place in the second stage and diffusion did not occur [29,30].

3.7. Effect of amount of SA impregnated on AC

The effect of amount of SA impregnated on AC on boron removal was examined by making the SA film layer thin.

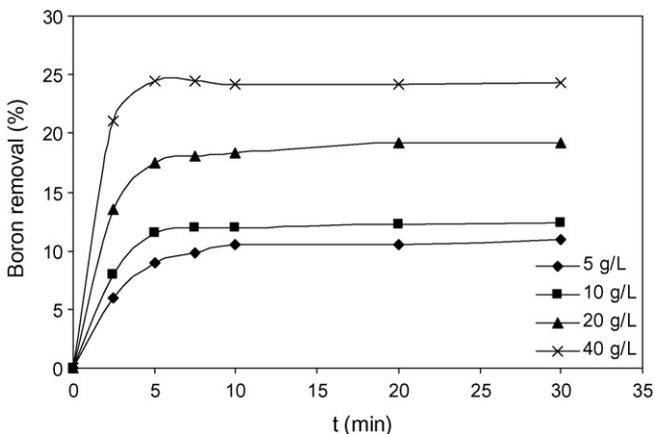


Fig. 7. The effect of adsorbent dose on boron removal.

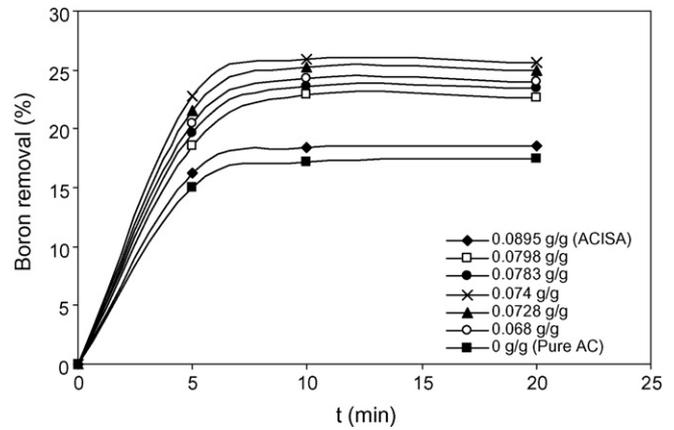


Fig. 8. The effect of SA amount on ACISA on boron removal.

Because salicylic acid dissolved in diethylether at room temperature, SA film layer of ACISA was made thin by stirring in 100, 200, 300, 400, 500, 600, 800 and 1000 ml-diethylether, respectively. It was natural that as volume of diethylether used increased, thickness and amount of SA on ACISA decreased, and so, the thinner SA film layer on ACISA and the lesser the amount of SA impregnated on AC decreased, surface areas of ACISAs increased, as seen in Table 1. Data obtained with ACISAs having various amounts of SA and AC unimpregnated with SA is given in Fig. 8. As seen in this figure, boron removal increases as amount of SA decreases and then decreases. Also, due to reaching to equilibrium at 10 min for boron adsorption in experiments, data under conditions which reaction time was taken constant 10 min and solid-to-liquid ratio 20 g/L, initial boron concentration 25 ppm, shaking rate 175 rpm and temperature 30 °C were compared both for AC impregnated and unimpregnated with SA in Fig. 9.

It was seen in Figs. 8 and 9 that as amount of SA on ACISA was decreased, boron removal increased at first and after it reached to a maximum, decreased. Although the surface areas of AC and ACISA were 609 and 559 m<sup>2</sup>/g, respectively, removal obtained by stock ACISA was bigger than that of AC. Also, after treatment with diethylether, ACISA's surface area always was smaller than that of original AC. But, the biggest removal

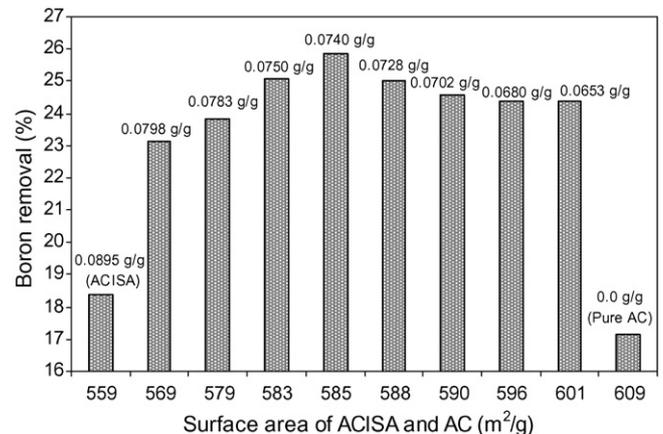


Fig. 9. Effect of SA amount on ACISA on boron removal.

was obtained with ACISA having surface area of 585 m<sup>2</sup>/g (obtained with 400 ml-diethylether), smaller than that of original AC (Table 1). As bigger volumes than 400 mL-diethylether were used to remove SA on ACISA, boron removals began to decrease.

This situation can be evaluated from two points of view. The first is that when AC was impregnated with SA, some small pores and channels in AC were plugged with SA. When ACISA was washed with diethylether, some of pores and/or channels would be opened, surface area would increase and more boron would be adsorbed. Using more than 400 ml-diethylether might remove some of SA on AC and sites that not contained SA on AC surface might be formed. This case was verified by thickness of SA calculated by Eq. (1). Secondly, because hydrophob and hydrophil ends turning towards of multilayer SA are opposite each other in each layer, it is under consideration to reach to layers supplying the most appropriate conformation.

#### 4. Conclusion

In this study, ACISA was used instead of AC in order to remove boron. The effects of parameters such as pH, temperature, shaking rate, adsorbent (ACISA) dose, SA amount on AC and initial boron concentration were examined on boron removal. Boron removal increased with increasing adsorbent amount, temperature and pH, decreasing initial boron concentration. As amount of SA on ACISA lowered to 0.0740 g/g, the removal increased, and then, the efficiency decreased with becoming lower than 0.740 g/g of SA amount. Results showed that in order to increase boron removal, AC having large surface area should be used for impregnation with SA. Shaking rate was no effect on removal efficiency.

Here a cyclic molecule forms between –OH and –COOH ends of SA with boric acid molecule due to conformation convenience. This molecule, having lactone structure, is the most stable ring which will be able to form as seen in Eq. (5).

Here process has two stages, first impregnating SA on AC and second boron removal by ACISA. It is accepted that the first stage which SA is impregnated on AC is a physical adsorption. The second stage in which formation between –COOH and –OH groups with boric acid or borate ion, being a six-member lacton is a chemisorption. Chemical reaction here were confirmed with literature data, too [20,21]. Also, that Arrhenius graph gave an activation energy of 54.85 kJmol<sup>-1</sup> verified that the process was a chemisorption [28].

In taking into consideration submitted data and mechanistic explanations above, it can be said that ACISA can be used to remove boron from aqueous solutions. Especially, after boron is chemisorbed, that adsorbent regeneration becomes easy as seen in Eq. (7) is important from the point of view of economy.

#### References

- [1] U. Schide, E. Uhlemann, Extraction of boric acid from brines by ion exchange, *Int. J. Miner. Process.* 32 (1991) 295–309.
- [2] P.C. Willem Duyvestern, R. Lastra Manuel, L. Houyuan, Boron recovery from geothermal brines, US Patent 5,236,491 (1993).
- [3] A. Hanay, R. Boncukçuoğlu, M.M. Kocakerim, A.E. Yılmaz, Boron removal from geothermal waters by ion exchange in a batch reactor, *Fresenius Environ. Bull.* 12 (10) (2003) 1190–1194.
- [4] R. Boncukçuoğlu, A.E. Yılmaz, M.M. Kocakerim, M. Çopur, An empirical model for kinetics of boron removal from boron-containing wastewater by ion exchange in a batch reactor, *Desalination* 160 (2004) 159–166.
- [5] A.E. Yılmaz, R. Boncukçuoğlu, M.T. Yılmaz, M.M. Kocakerim, Adsorption of boron-containing wastewaters by ion exchange in a continuous reactor, *J. Hazard. Mat.* 117 (2005) 221–226.
- [6] Mj.D. Ristic, Lj. Rajakovic, Boron separation from water onto ion exchange resin impregnated by organic compounds, *Sep. Sci. Technol.* 31 (20) (1996) 2805–2814.
- [7] F. Kahraman, Effect of sodium, calcium, magnesium and chloride ions on the solvent extraction of boron from aqueous solutions, *Solvent Extr. Ion Exch.* 13 (2) (1995) 323–332.
- [8] W.D. Peterson, Extraction of boron from aqueous solutions with salicylic acid derivatives, US Patent 3,741,731 (1973).
- [9] M. Karakaplan, S. Tural, M. Sünkür, H. Hoşgören, Effect of 1,3-diol structure on the distribution of boron between CHCl<sub>3</sub> and aqueous phase, *Sep. Sci. Technol.* 38 (2003) 8.
- [10] B. Egneus, L. Uppström, Extraction of boric acid with aliphatic 1,3-diols and other chelating agents, *Anal. Chim. Acta* 66 (2) (1973) 211–229.
- [11] Lj.V. Rajakovic, Mj.D. Ristic, Sorption of boric acid and borax by activated carbon impregnated with various compounds, *Carbon* 34 (6) (1996) 769–774.
- [12] N. Öztürk, D. Kavak, Boron removal from aqueous solutions by adsorption using full factorial design, *Fresenius Environ. Bull.* 12 (2003) 1450–1456.
- [13] D. Peak, W.G. Luther, D. Sparks, ATR-FTR spectroscopic studies of boric acid adsorption on hydrous ferric oxide, *Geochim. Cosmochim. Acta* 67 (14) (2003) 2551–2560.
- [14] P. Keren, D. Sparks, Effect of pH and ionic-strength on boron adsorption by pyrophyllite, *Soil Sci. Soc. Am. J.* 58 (4) (1994) 1095–1100.
- [15] A.E. Yılmaz, R. Boncukçuoğlu, M.M. Kocakerim, B. Keskinler, The investigation of parameters affecting boron removal by electrocoagulation method, *J. Hazard. Mat.* 125 (2005) 160–165.
- [16] N. Öztürk, D. Kavak, Adsorption of boron from aqueous solutions using fly ash: batch and column studies, *J. Hazard. Mat.* 127 (2005) 81–88.
- [17] N. Öztürk, D. Kavak, Boron removal from aqueous solutions by adsorption on waste sepiolite and activated waste sepiolite using full factorial design, *Adsorption* 10 (2004) 245–257.
- [18] J.G. Dawber, S.I.E. Green, An <sup>11</sup>B nuclear magnetic resonance study of the reaction of the tetrahydroxy borate ion with polyhydroxy compounds, *J. Chem. Soc., Faraday Trans. I* 82 (1986) 3407–3413.
- [19] J.C. Dawber, S.I.E. Green, S. Gabrail, A polarimetric and <sup>11</sup>B and <sup>13</sup>C nuclear magnetic resonance study of reaction of tetrahydroxyborate ion with polyol and carbohydrates, *J. Chem. Soc. Faraday Trans. I* (1988) 41–56.
- [20] R.P. Oertel, Raman study of aqueous monoborate-polyol complexes. Equilibria in monoborate-1,2-ethanediol system, *Inorg. Chem.* 11 (3) (1972) 544–549.
- [21] M. Van Duin, J.A. Peters, A.P.G. Kieboom, H. Van Bekkum, Studies on borate esters, I: The pH dependence of the stability of esters of boric acid and borate in aqueous medium as studied by <sup>11</sup>B NMR, *Tetrahedron* 40 (15) (1984) 2901–2911.
- [22] L.A. Randal, J.C. King, Separation of Glycols from aqueous solution via complexation with boronic acid, MS Thesis, Lawrence Berkeley Laboratory University of California, Applied Science Division, Berkeley, California, 1991.
- [23] P.H. Kemp, *The Chemistry of Borates*, Part I, Borax Consolidated Ltd., London, 1956.
- [24] <http://chemport.cas.org/cgi-bin/sdcgi?APP=cp-scifinder&SERVICE=&CLI=scifinder&SID=1685415-0450266006-103&FID=REDISPLAY&LANG=english&R=647724>.
- [25] E. Svarcs, V. Grundsteins, I. Vitols, The application of thermal analysis to investigation of the interaction of boric acid with salicylic acid derivatives, *Therm. Anal. Proc. Int. Conf.* (1982) 803–808.

- [26] Grundsteins, E. Svarcs, Reaction in the boric acid–salicylic acid system, *Latvijas PSR Zinatnu Akademijas Vestis Kimijas Serija* 2 (5) (1978) 131.
- [27] N. Bachelier, C. Chappey, D. Langevin, M. Metayer, J.F. Verchere, Facilitated transport of boric acid by 1,3-diols through supported liquid membranes, *J. Membr. Sci.* 119 (2) (1996) 285–294.
- [28] G. Wedler, *Chemisorption: An Experimental Approach*, Translated by D.F. Klemperer, Butterworths, London, 1976.
- [29] O. Levenspiel, *Chemical Reaction Engineering*, 3rd ed., John Wiley and Sons, New York, 1999.
- [30] F. Habashi, Exploiting the boundary layer, *Educ. Chem.* 28 (2) (1991) 52–54.