



Optimisation of boric acid production plant wastewater treatment by calcium hydroxide and advanced treatment by ion exchange

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Abstract

The Emet boric acid production plant in Türkiye produces boric acid from the reaction of colemanite ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$) with sulphuric acid (H_2SO_4). Sulphate, arsenic (III + V) and boron are released with the plant wastewater to the wastewater dam. This study aims to treat this boric acid production plant wastewater using calcium hydroxide in a batch reactor. The concentrations of the contaminants were 3956 mg/L sulphate, 2541 mg/L boron and 36.4 mg/L total arsenic (III + V). The boron removal kinetic studies were conducted to obtain the optimum parameter intervals for the application of the central composite experimental design method to remove these contaminants. The optimum conditions in the kinetic studies for boron removal were obtained as natural wastewater pH (5.32–5.68), temperature (20 °C), stirring speed (300 rpm), calcium hydroxide dosage (15 g/L) and time (90 min). Maximum boron removal obtained from the kinetic studies was calculated as 90.7%. The kinetics of boron removal obeyed the second-order model. Sulphate, boron and arsenic removal in the optimisation studies were calculated as 23.94, 87.94 and 98.36% in optimum boron removal conditions, respectively. An ion exchange treatment was applied to the calcium hydroxide treated wastewater containing boron and sulphate residues for ~ 100% removal.

Keywords Arsenic · Boron · Calcium hydroxide · Ion exchange · Sulphate

Introduction

Boric acid can be produced by the reaction of the borates, namely ulexite, pandermite, colemanite and kernite, with strong or weak acids (Okur et al. 2002; Kuşçay and Bulutçu 2011). In Türkiye and Europe, boric acid is obtained by the reaction of colemanite, a calcium borate, with sulphuric acid, and the gypsum-containing boron is the by-product of this reaction (Örs et al. 2001; Aydın 2006). Türkiye is one of the biggest borate mining countries and possesses 61% of the world's borate deposits (Korkmaz et al. 2016). In Türkiye, the colemanite deposits are located in Emet, Bigadiç, Kırka and Kestelek regions (Koç et al. 2017; Akkurt et al. 2022). The impurities of Emet colemanite are ulexite, magnesium borate, calcium carbonate, montmorillonite clay,

magnesium carbonate, sodium silicate, strontium carbonate, iron oxide, silicon oxide, orpiment (As_2S_3), realgar (As_2S_2) and probably calcium arsenate (Örs et al. 2001). The wastewater production steps in the Emet boric acid production plant can be summarised as follows.

1. Colemanite, a calcium borate, is excavated in the Emet mine and transferred by hand sorting from impurities like arsenic minerals and transferred to the crushing unit.
2. After the crushing of colemanite, it is transferred to a reaction unit with sulphuric acid, and saturated boric acid solution is obtained (Aydın 2006).
3. Then, this saturated solution with 88–90 °C temperature is filtered for separation of the gypsum, a calcium sulphate (Kuskay, and Bulutcu, 2011).
4. Thereafter, the filtered saturated boric acid solution is crystallised (35–46 °C) (Örs et al. 2001; Kuşçay and Bulutçu (Kuskay, and Bulutcu, 2011) and the obtained poor boric acid solution is either returned to the colemanite dissolution process or mixed with gypsum for storage in the wastewater dam (Wastewater 1) (Kuskay, and Bulutcu, 2011).

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5. The crystallised crystals are centrifuged and washed during centrifugation, and this crystal washing water is mixed with poorly crystallised process water and gypsum (Wastewater 1) (Aydin 2006), and the end wastewater (End wastewater) was obtained by mixing Wastewater 1 and crystal washing water and is stored in the wastewater dam. The end wastewater is used in the present study for treatment. The used wastewaters in the present study were taken from the process exiting pipe and not from the wastewater dam.

This wastewater is stored in a waste dam, but ecological risk continues for the disasters to be realised and the dam wastewater volume increases. The detailed flow diagram of the boric acid production is given elsewhere (Gönen et al. 2022). Therefore, the treatment of this wastewater is necessary. The Emet boric acid plant wastewater contains 3956 mg/L sulphate, 2541 mg/L boron and 36.34 mg/L total arsenic (III + V) (Korkmaz 2023). The by-product gypsum ingredients are mainly boric acid, arsenic sulphur (As_2S_3 and As_2S_2), montmorillonite clay, calcium arsenate and other impurities (Arslan et al. 1999; Örs et al. 2001).

Boron is distributed in nature due to either anthropogenic or natural reasons (Remy et al. 2005). The natural sources of boron are boron ores, geothermal springs, volcanoes and ocean aerosols in the atmosphere (Tariq and Mott 2007; Korkmaz et al. 2016). Some anthropogenic sources of boron include detergents, boric acid and borax production, and discharge of boron chemicals. The industrial consumption of boron increases as it has unique properties such as hardness, anti-microbial, fire resistance and neutron absorption (Bayar 2001; Korkmaz et al. 2016). Industries utilising boron include glass and glassware production, soap and detergent formulation, porcelain and enamel manufacturing, agriculture, and metallurgy (Bayar 2001; Korkmaz et al. 2016; Akkurt et al. 2022). The $\text{p}K_a$ of boric acid is 9.22 (weak acid), and boron has complex solution chemistry (Korkmaz et al. 2017). In the aqueous phase, different boron molecules are formed by polymerisation such as $\text{B}(\text{OH})_3$, $\text{B}(\text{OH})_4^-$, $\text{B}_2\text{O}(\text{OH})_5^-$, $\text{B}_3\text{O}_3(\text{OH})_4^-$, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ and $\text{B}_5\text{O}_6(\text{OH})_4^-$ (Na and Lee 1993; Tsai and Lo 2015; Korkmaz 2023). Molar fraction of the polyborates increases with decreasing temperature for boron concentrations above 0.025 M (Anderson et al. 1964; Na and Lee 1993). It is well known that the physico-chemical methods are generally effective for boron, sulphate and arsenic (III + V) removal from wastewaters. For the removal of boron of which concentrations are in the range of 300–1000 mg/L, inorganic sorbents such as $\text{M}(\text{OH})_n$, $\text{M} = \text{Ca, Al, Fe, Sn, Ti, Mn, Ni, Mg, Zn}$ and Zr , can be applied (Sayiner, et al., 2008). Therefore, calcium hydroxide was selected for sulphate, boron and arsenic removal from boric acid production plant wastewater.

Sulphate is present in the wastewaters as bare negative divalent sulphate anion. Boron is present as boric acid due to natural pH (5.32–5.68). Arsenic is present as arsenite and arsenate molecules. Sulphate, boron and total arsenic concentration ranges in the treated wastewater are based on the purity of the colemanite ore and its arsenic impurity.

Public water systems are regulated with a current drinking-water standard for arsenic at 10 ppb under the Safe Drinking Water Act (EPA 2009; WHO 2022). Arsenic is classified as a group 1 carcinogen by International Agency of Research on Cancer (IARC) as there are sufficient experimental and epidemiologic studies supporting causation of skin, bladder and lung cancers (Roha et al. 2017).

Also, the effects of exposure to arsenic through drinking water include various skin lesions, neurological effects, hypertension, cardiovascular diseases, respiratory disorders, diabetes, oedema, gangrene, ulcers, skin cancer, bladder and other types of cancer, miscarriage, stillbirth, premature birth, weakness, weight loss, numbness, anaemia and damage to the immune system. In general, the inorganic arsenic species (As (III) and As (V)) are more toxic than the organic species (Can 2010).

Acute signs of boron toxicity in humans have been reported as nausea, vomiting, diarrhoea, dermatitis and dizziness, and chronic signs of toxicity have been reported as decreased appetite, nausea, weight loss, decrease in sexual activity and decrease in low seminal volume sperm motility (Çakır, 2022). An acceptable range for boron consumption, as recognised by the World Health Organization, is 1–13 mg/day (Çakır, 2022). Boron permissible concentration in drinking water is 2.4 mg/L (Tagliabue et al. 2014; WHO 2022; De Azevedo et al. 2024), and that for irrigation water was suggested to be below 0.75 mg/L (Guo et al. 2013). The industrial boron discharge value for developing countries is 1 ppm (Acton 2013).

Uncontrolled observations show that sulphate in drinking water at concentrations exceeding 500–700 mg/L causes diarrhoea (Heizer et al. 1997; Korkmaz 2023). In general, the average daily intake of sulphate from drinking water, air and food is approximately 500 mg, food being the major source (WHO 2022). However, in areas with drinking-water supplies containing high levels of sulphate, drinking water may constitute the principal source of intake (WHO 2022). The reason for not establishing a guideline value is that sulphate is not of health concern at levels found in drinking water (WHO 2022). Sulphate and inorganic arsenic species can be removed by metal hydroxides using the precipitation method (Benatti et al. 2009; Nurmesniemi et al. 2022). Boron molecules are toxic for human health at above permissible levels. In Türkiye, according to the Regulation on the Control of Pollution Caused by Hazardous Substances in Water and the Environment, boron, arsenic and sulphate discharge standards are given as 3, 0.1 and 90 mg/L,

respectively (Official Gazette Date: 26.11.(2005) Official Gazette Number: 26005).

Concentrations of B in surface freshwaters are typically $<0.1\text{--}0.5$ mg/L; much higher concentrations are measured in some areas, depending on the geochemical nature of the drainage catchment. Boron accumulates in both aquatic and terrestrial plants, but it does not appear to be biomagnified through the food chain (Howe 1998).

Plants are important vectors for arsenic accumulation in the environment, as they can take up arsenic from the soil and water and translocate it to their tissues. Arsenic uptake by plants occurs through the roots, and the amount of arsenic that a plant can accumulate depends on a variety of factors, including the concentration of arsenic in the soil and water, the pH of the soil and the plant species (De and Roy 2023). Sulphate is accumulated by plants and microorganisms and is moved up to the food chain.

The stability of the colloids in a suspension is mainly dependent on the electrostatic surface potential known as the zeta potential. The zeta potential of the colloids is dependent on parameters like solution pH and solid-to-solution ratio (Yükselen and Kaya 2003). Calcium hydroxide is dissolved in solutions up to solution pH value of 12 by buffering the pH and remains in the solution as Ca^{2+} and $\text{Ca}(\text{OH})^+$, $\text{Ca}(\text{OH})_2$ (Ersoy et al. 2010).

Several studies have been reported for boron, arsenic and sulphate removal by calcium hydroxide. Yu and coworkers reported the optimum boron removal (59.1%) by calcium hydroxide for 400 mg/L, 250 mL water volume, 0.5 g dosage, pH 10.5, 120 min and 80 °C temperature conditions (Yu et al. 2022). In another study, it was reported that the boron removal by calcium hydroxide was strongly decreased with the presence of sulphate anion (Tsai and Lo 2011). Tsai and coworkers reported that the boron removal by submicron calcium hydroxides obtained by precipitation method using calcium chloride and calcium nitrate tetrahydrate did not change when calcium hydroxide dosage is increased (Tsai and Lo 2015). Remy and coworkers reported that boron removal did not change when increasing the calcium hydroxide amount above 45 g/L up to 75 g/L (Remy et al. 2005). The optimum removal parameters of sulphate removal by calcium hydroxide (CH) and sodium aluminium oxide (SA) mixture were reported as a molar ratio of CH/SA of 2, initial pH value 5, precipitant dosage of 15 g/L, reaction time of 20 min, and reaction temperature of 55 °C (Yu et al. 2018). In arsenic removal from waters, it was reported that calcium hydroxide could remove arsenic effectively and different combination effects of MgO , $\text{Mg}(\text{OH})_2$, MgCO_3 , CaO and CaCO_3 with calcium hydroxide were interpreted for arsenic removal (Sugita et al. 2023). According to Akkurt and coworkers, boron removal from the wastewater of Eti Maden Kirka Boron Operation was reported by using single-stage and two-stage treatment with calcium hydroxide and

aluminium sulphate and the initial concentration (2752 ppm) could be reduced to 250 ppm boron (Akkurt et al. 2022).

The response surface methodology (RSM) was first defined by Box and Wilson (Box and Wilson 1951; Turan and Altundağ, 2011); Süzen 2023). They exposed the experimental design matrix giving the optimum response by means of a very low experimental run. Generally, the RSM analysis is formed from three stages, namely the parameter elimination study that provides the low run, the ANOVA of the factors for the regression model development and the analysis of factor levels to obtain the optimum conditions (Süzen 2023). The general model in RSM analysis can be obtained by ANOVA (Urréjola-Madriñán et al. 2022; Korkmaz 2023; Süzen 2023). The central composite experimental design is a tool of the response surface method of the Minitab 16.0 software.

The advantage of calcium hydroxide used for boric acid plant wastewater treatment is the recoverability of the formed reaction product in the boric acid production. The product of the reaction can be added again to the real production process gradually for boric acid production, and therefore, there will not be any by-product for discharge. Boron, arsenic and sulphate removal from wastewater of the Emet boric acid plant was studied using calcium hydroxide. Also, optimisation of the removal of these three pollutants was performed by the central composite design tool of response surface method.

In the literature, there are several studies for boron removal by calcium hydroxide from synthetically prepared boric acid solutions, but there is no study for boron, sulphate and arsenic removal from boric acid production plant wastewaters and kinetics of removal and optimisation. Also, the studied wastewater is complex and its removal is so important. The treatment of the wastewater by calcium hydroxide is new in the literature for this wastewater. The calcium hydroxide and ion exchange combination was so effective and central composite design of data was simple and usable for operation of real reactor.

The purpose of the study is to refine the wastewaters from the pollutants such as boron, sulphate and arsenic and to reuse the treated wastewater in the boric acid production. Thus, the wastewater could be refined from the pollutants by calcium hydroxide and ion exchange processes. The cost of the removal would be cheap due to low cost of calcium hydroxide and repeatedly usable ion exchange by regeneration. The optimisation study by central composite design showed the remaining pollutants in the wastewaters at optimum boron removal conditions. Thus, an ion exchange process could be proposed for the remaining boron and sulphate. Already, the arsenic could be removed by the calcium hydroxide treatment. The optimisation method was aimed to assess the remaining pollutants after treatment in a very effective and easy way as well as the parameter interaction

effects on the removal of the pollutants. The kinetics, thermodynamics and the diffusion mechanisms of removal were analysed. The XRD patterns and the SEM images of the raw calcium hydroxide and produced end-product were analysed for determination of the end-product material type. Thus, the treated wastewater can be reused in boric acid production.

Materials and methods

Equipment and chemicals used

A pH meter was used for pH and temperature measurements (WTW Multi 340i, Germany). A glass thermometer was used for the control of the solution temperatures. A glass-jacketed batch reactor was used for reaction (İldam, Türkiye). A mechanical stirrer was used for stirring the reactor content (Janke&Kunkel RW20 DZM). A Jar test device was used for optimisation experiments (Wise Stir Jar Tester). The calcium hydroxide used was a product of Merck company. A temperature-controlled water circulator was used for controlling the temperature of the working wastewater (Labo SM 3). The ion exchange resin used was the Selion SBA 2000 which is a strong base resin. The HCl and KOH used were the products of Merck company. A vacuum filtration device was used for filtration of the taken wastewater samples (Rocker 300). A glass automatic burette was used for titration of boron content. D-Mannitol was used for boron analysis (Merck). A magnetic stirrer was used during boron analysis (MTOPTS Hot Stirrer MS-300HS). ICP-OES device was used for arsenic and sulphate content analyses of the wastewater. Whatman filter paper was used in the wastewater sample filtration.

Boron removal kinetic experiments

pH effect experiments for boron removal

The solution pH is an effective parameter on boron ion type and removal yield by calcium hydroxide. The studied initial pH were between 1 and 8.5. A volume of 500 mL wastewater was taken by a balloon flask after filtration from gypsum and poured to 1.3 L reactor. For filtration, the sheet filter paper was used. Then, initial pHs were adjusted with 2.5 M HCl or KOH using a pH meter. Before pH adjustment, temperature (30 °C) of the wastewater was fixed by a water temperature controlling thermostat. Then, a weighted amount of calcium hydroxide (7.5 g) was added to the working solution and the stirring started (300 rpm) by a mechanical stirrer. At certain time intervals (0–150 min), a 4 mL wastewater was taken and filtered with Whatman filter paper using a vacuum filtration device and filtration tubes. The filtered water samples that would be analysed, were acidified using

2.5 M HCl (1:1 extent) to stop the probable reaction (Remy et al. 2005). Thereafter, 1 mL supernatant wastewater was taken and analysed for boron. The times for boron removal kinetics were 5, 15, 30, 60, 90, 120, 150 min and after taken of the samples, they were filtered immediately, acidified and boron content was analysed.

Calcium hydroxide amount effect experiments for boron removal

The calcium hydroxide amount is an effective parameter on boron ion type and removal yield by effecting operation pHs and active adsorbing site number. The studied calcium hydroxide amounts were between 5 and 12.5 g. A volume of 500 mL wastewater was taken by a balloon flask after filtration from gypsum and poured to 1.3 L reactor. For filtration, the sheet filter paper was used. The initial pHs were natural wastewater pHs (5.38–5.64). Temperature (30 °C) of the wastewater was fixed by a water temperature controlling thermostat. Then, a weighted amount of calcium hydroxide between 5 and 12.5 g was added to the working solution and the stirring started by a mechanical stirrer (300 rpm). At certain time intervals (0–150 min), a 4 mL wastewater was taken and filtered with Whatman filter paper using a vacuum filtration device and filtration tubes. The filtered water samples were acidified using 2.5 M HCl (1:1 extent) to stop the probable reaction (Remy et al. 2005). Thereafter, 1 mL supernatant wastewater was taken and analysed for boron. The times for boron removal kinetics were 5, 15, 30, 60, 90, 120, 150 min and after taken of the samples, they were filtered immediately, acidified and boron content was analysed.

Temperature effect experiments for boron removal

The temperature is an effective parameter on boron ion type and removal yield. The studied temperatures were between 20 and 50 °C. A volume of 500 mL wastewater was taken by a balloon flask after filtration from gypsum and poured to a 1.3-L reactor. For filtration, the sheet filter paper was used. The pH were natural pH (5.38–5.47). Temperature of the wastewater was fixed to desired temperature by a water temperature–controlling thermostat. Then, 7.5 g of calcium hydroxide was added to the working solution and the stirring started by a mechanical stirrer (300 rpm). At certain time intervals (0–150 min), 4 mL of wastewater was taken and filtered with Whatman filter paper using a vacuum filtration device and filtration tubes. The filtered water samples were acidified using 2.5 M HCl (1:1 extent) to stop the probable reaction (Remy et al. 2005). Thereafter, 1 mL of supernatant wastewater was taken and analysed for boron content. The times for boron removal kinetics were 5, 15, 30, 60, 90, 120

and 150 min, and after taking the samples, they were filtered immediately, acidified and the boron content analysed.

Stirring speed effect experiments for boron removal

Stirring speed is an effective parameter on the liquid film resistance surrounding the calcium hydroxide particle. The studied stirring speeds were between 150 and 375 rpm. A volume of 500 mL wastewater was taken using a balloon flask after filtration from gypsum and poured into a 1.3-L reactor. For filtration, sheet filter paper was used. The initial pH were natural pH (5.3–5.4). Temperature (30 °C) of the wastewater was fixed by a water temperature–controlling thermostat. Then, 7.5 g of calcium hydroxide was added to the working solution and the stirring started by a mechanical stirrer. At certain time intervals, a 4-mL wastewater sample was taken and filtered with Whatman filter paper using a vacuum filtration device and filtration tubes. The filtered water samples were acidified using 2.5 M HCl (1:1 extent) to stop the probable reaction (Remy et al. 2005). Thereafter, 1 mL of supernatant wastewater was taken and analysed for boron content. The times for boron removal kinetics were 5, 15, 30, 60, 90, 120 and 150 min, and after taking the samples, they were filtered immediately, acidified and the boron content analysed.

Boron, sulphate and total arsenic (III) analysis procedures

The characterisation of the wastewater is given in Table 1. The Emet boric acid plant wastewater contains only boron, arsenic, sulphate and harmless cations as seen in Table 1. The sulphate and the total arsenic (III) concentrations were measured using the ICP-OES device. Sulphate analysis was realised based on sulphur calibration curve at a range of 50–2000 ppb concentration and total arsenic (III) concentration was measured for calibration curve of 50–1000 ppb concentration. To prepare the reducing solution for the total arsenic (III) analysis, 5 g pure grade ascorbic acid was mixed with 5 g potassium iodide, and this mixture was dissolved in 100 mL pure water in a polypropylene vessel. For the total arsenic (III) analysis procedure, 8 mL of sample was taken in a 15-mL centrifuge tube. Then, 1 mL concentrated HCl and 1 mL reducing solution were added into the vessel. The treated solution was then allowed to stand for 70–90 min for completion of the reduction. After the prereduction, the solutions were analysed. The aim of the prereduction was to reduce the arsenic (V) to arsenic (III) because the wastewater contains both arsenic (V) and arsenic (III). The procedure for boron analysis was as follows (Foote 1932; Korkmaz et al. 2020a): a volume of 1 mL acidified wastewater sample (1:1 extend) was transferred into a 100-mL beaker, 50 mL pure water was added, pH of the acidic solution was adjusted to 7.6 and D-mannitol was added up to constant pH value.

Table 1 Characterisation of Emet boric acid plant wastewater

Parameter	Value
pH	5.32–5.68
Conductivity (mS)	4.67
M.O. alkalinity (mg/L CaCO ₃)	120
Na ⁺ (mg/L)	172.0
K ⁺ (mg/L)	31.0
Mg ²⁺ (mg/L)	518.0
Ca ²⁺ (mg/L)	496.0
Zn ²⁺ (mg/L)	1.3
Mn ²⁺ (mg/L)	3.7
SO ₄ ²⁻ (mg/L)	3956
Boron (mg/L)	2541
T-As (mg/L)	36.4
As ⁺⁵ (mg/L)	23.8
As ⁺³ (mg/L)	12.6
Al ³⁺ (µg/L)	< 12.43
Cr ³⁺ (µg/L)	< 6.50
Co ²⁺ (µg/L)	< 10.50
Pb ²⁺ (µg/L)	< 8.29
Cd ²⁺ (µg/L)	< 6.68
Cu ²⁺ (µg/L)	< 6.73
Fe ³⁺ (µg/L)	< 7.15
Ni ²⁺ (µg/L)	< 6.45

Then, this solution was again titrated to pH 7.6 with 0.05 N KOH. One millilitre of 0.05 N KOH solution is equal to 1.741 mg B₂O₃. The KOH solution was standardised against a 500-mg/L boron solution daily (Korkmaz et al. 2020a). The calcium hydroxide used was purchased from Merck, and its standards are constant. All the experiments were carried out at ambient room atmosphere. The concentration of boron was calculated using the following equation:

$$(\text{Boron, mg/L}) = \frac{(V_1 - V_2) \times 0.540675 \times 1,000 \times 2 \times Sf}{V_3} \quad (1)$$

Here, V_1 is the volume of consumed base (mL), Sf is standardisation factor, V_2 is base consumption for pure water (about 0.05 mL) and V_3 is the volume of taken boron solution (1 mL). Boron, arsenic and sulphate removal percentages were calculated using the following equation:

$$\eta = \frac{(C - Ce)}{C} \times 100 \quad (2)$$

Here, η is the boron, sulphate or arsenic removal percentage (%). C is the initial concentration of boron, sulphate or total arsenic (III) (mg/L). C_e is the measured concentrations of boron, sulphate and total arsenic (III) (mg/L) after treatment. The pore diameter of calcium hydroxide was between 8 nm and 91 µm. The average

pore diameter was 1339.4 nm. The particle size fraction of calcium hydroxide was measured by sieve analysis during 15 min as > 1.44 mm (2.84%), 850 μm to 1.4 mm (19.15%), 600 μm to 850 μm (3.17%) and < 600 μm (74.84%). The standard deviations on boron, sulphate and arsenic analyses were obtained as maximum 6%, 5% and 7%, respectively. The analysis results can be expected to change around these error values. The pH could be measured ± 0.15 and temperature could be adjusted to ± 1.5 °C accuracy using a pH meter. The stirring speeds are changed ± 7 rpm. Therefore, there is not any significant effect of fluctuations on the results. There is a significant factor such as conservation of calcium hydroxide from open atmosphere, and I conformed to the criterion.

Central composite design experiments for boron, sulphate and arsenic removal

The central composite design experiments were carried out using 500 mL of wastewater in a 1.3-L glass-jacketed reactor at 300 rpm stirring speed and 150 min operation time. The experimental matrix parameters were initial pH (1–9), temperatures (20–60 °C) and calcium hydroxide amounts (2.5–12.5 g). The central composite design experiments were performed according to the experimental matrix conditions determined by Minitab 16.0 software. While the experimental conditions of central composite design were being determined, the optimum conditions of boron removal kinetic experiments were taken into consideration. The optimum operation values were 300 rpm and 150 min, and the other parameter values such as pH, temperature and calcium hydroxide amounts were changed. The advantage of central composite design is the numerical results of optimisation. The central composite design is a tool of response surface optimisation method. In the ANOVA, sulphate, boron and total arsenic (III) removal efficiencies were optimised and analysed. The experimental procedures were identical with the pH, temperature and dosage effect experiments given in the above. The experiments were carried out using a Jar test device which is operatable at 300 rpm stirring speed.

Ion-exchange experiments of boron and sulphate residue removal after calcium hydroxide treatment

After treatment of boron, sulphate and arsenic using calcium hydroxide at conditions of pH 5.58, 15 °C, 200 rpm, 7.5 g and 150 min, the sulphate residue removal by Selion SBA 2000 resin was carried out at pH 8, 20 °C, 200 rpm, 50 mL and 24 h, and boron residue removal by Purolite S 108 resin was carried out at pH 8, 20 °C, 200 rpm, 3.5 h and 50 mL. Thus, ~ 100% boron and sulphate removal could be realised by calcium hydroxide treatment following ion exchange. The

ion-exchange experiments were carried out for sulphate and boron residues in an incubator shaker using 50 mL treated wastewaters by calcium hydroxide.

Results and discussion

pH effect on boron removal

The wastewater of Emet boric acid production plant in Türkiye has a pH value of 5.32–5.69. Generally, boron-containing waters such as geothermal waters, sea waters, alkaline lake waters and boron processing industrial wastewaters have changing pHs, temperatures and concentrations (Mahdy et al. 2004; Kabay et al. 2007, 2013; Imbernón-Mulero et al. 2022). These conditions affect the boron ion type in these waters as the boron ion type changes with boron concentration, temperature and pH (Anderson et al. 1964; Yılmaz 2009; Korkmaz 2023). Boron, sulphate and total arsenic (III) concentration in the boric acid plant wastewater are 3956 mg/L SO_4^{-2} , 2,541 mg/L boron and 36.4 mg/L total arsenic (III + V). Arsenic types in the wastewater are arsenite and arsenate molecules. The studied parameters for boron removal from the boric acid plant wastewater were pH 1–8.5, dosage 15 g/L, temperature 30 °C, stirring speed 300 rpm, boron concentration

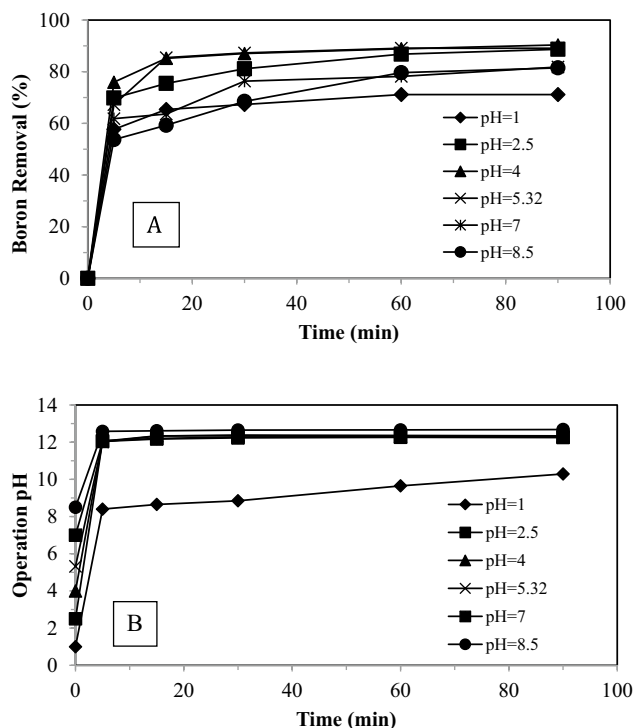


Fig. 1 A pH effect on boron removal by calcium hydroxide (calcium hydroxide amount 15 g/L, 30 °C, 300 rpm, 500 mL wastewater volume). B Operation pH change during removal

2541 mg/L and 500 mL wastewater volume. As can be seen in Fig. 1A, optimum initial wastewater pH was determined as natural pH (5.32). The change of solution pH during removal by calcium hydroxide is given in Fig. 1B. During the operation of the batch reactor for boron removal by calcium hydroxide, the end-point wastewater pH resulted between 10.32 and 12.68 for initial pH (1–8.5), respectively. The operation solution pH for 5–150 min at initial pH value of 1 changed between 8.4 and 10.32 at which boron ion types were borate molecules such as $\text{B}(\text{OH})_3$, monoborate $\text{B}(\text{OH})_4^-$, diborate $\text{B}_2\text{O}(\text{OH})_5^-$, triborate $\text{B}_3\text{O}_3(\text{OH})_4^-$, tetraborate $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ and pentaborate $\text{B}_5\text{O}_6(\text{OH})_4^-$ (Yılmaz 2009; Korkmaz et al. 2020a; Korkmaz 2023). On the other hand, the end-point operation pH values for starting pH (2.5–8.5) at 5–150 min changed between 12.01 and 12.68 and the boron type for these pHs was only monoborate anion. It was reported that the optimum pH value is 10 for electrochemically generated aluminium hydroxide. In that study, the reason of this optimum pH value of 10 can be considered as the low hydroxyl ion competition for boric acid and monoborate adsorption (Yılmaz 2009). Also, optimum boron removal by $\text{Al}(\text{OH})_3$ was reported to occur at pH between 8 and 9 and the reason was considered as related to boric acid and monoborate competition with hydroxyl ions for adsorption (Korkmaz et al. 2020b). In the present study, the decrease of removal above initial pH value of 5.32 is due to hydroxyl competition with boron for adsorption onto calcium hydroxide (Tsai and Lo 2015). Calcium hydroxide has pH 12.9 of point of zero charge value, and this value is high from operation pH of the present study and causes hydroxyl ion competition due to positive calcium hydroxide surface (Tsai and Lo 2015; Akkurt et al. 2022). Therefore, the studied calcium hydroxide had positive surface charge for initial pH between 1 and

8.5. The low efficiency of low pH is also due to dissolution of calcium hydroxide. Boron removal percentages of 1, 2.5, 4, 5.32, 7 and 8.5 pH were 71.15, 86.79, 88.88, 89.09, 85.45 and 81.48%. The dissolution of calcium hydroxide for 1, 2.5 and 4 pH were 3.704, 0.1 and 0.004 g, and thereafter it can be negligible. Therefore, the effect of polyborates against monoborate is unclear due to formation of polyborates at only initial pH of 1 and high dissolution of calcium hydroxide at pH of 1. At above initial pH of 1 in the present study, polyborates did not form. The boron ion types at various pH and concentrations are given in Figs. 2 and 3. The theoretical change of calcium ion concentration in the synthetic solution against solution pH is given in Fig. 4. In a study, optimum boron removal pH was reported as 13 at parameters of 500 mg/L boron, 0.5 g/30 mL calcium hydroxide dosage, temperature 130 °C and 0.5 h operation time (Tsai et al. 2011). The reason of optimum pH (13) was the operation temperature and solid-to-solution ratio influencing the dissolution of calcium hydroxide. In another study, optimum initial solution pH was 11 at parameter conditions of 0.5 g calcium hydroxide dosage, temperature 50 °C, 60 min operation time, 400 mg/L boron concentration and 250 mL solution volume. The reason for this optimum initial solution pH (11) was the temperature and solid-to-solution pH affecting the dissolution of calcium hydroxide (Yu et al. 2022). This is because calcium hydroxide presence could not be buffered by the pH for solid calcium hydroxide presence in the solutions at low dosages.

Temperature effect on boron removal

The temperature effect on the reactions shows generally endothermic or exothermic trends for the removal of pollutants. The removal percentage of endothermic processes

Fig. 2 The molecule types of boron in 100 mM (6.183 g/L boric acid) concentration at changing pH (I: 4.67 mS, 25 °C)

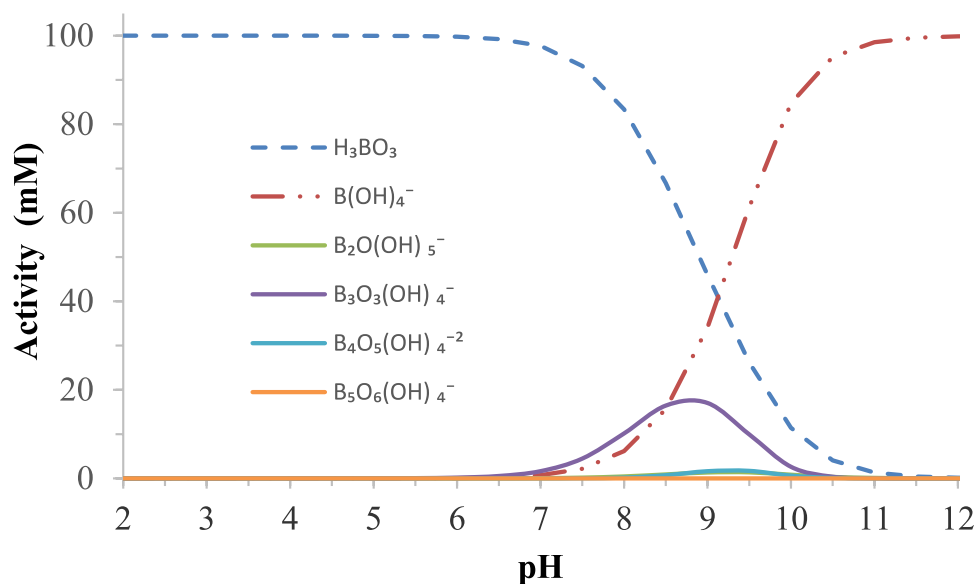


Fig. 3 The molecule types of boron in 250 mM (15.458 g/L boric acid) concentration at changing pH (I: 4.67 mS, 25 °C)

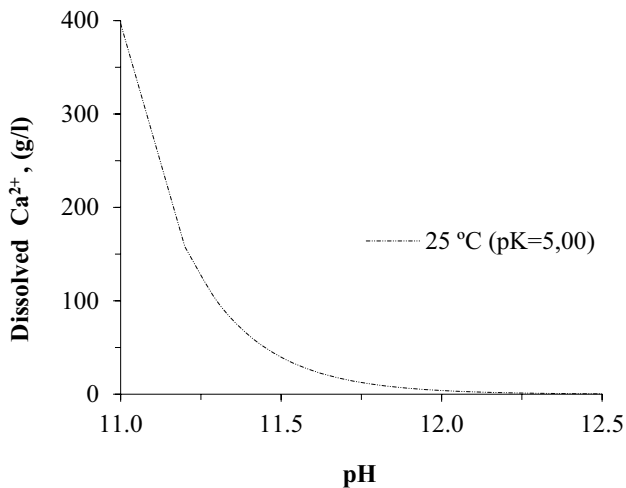
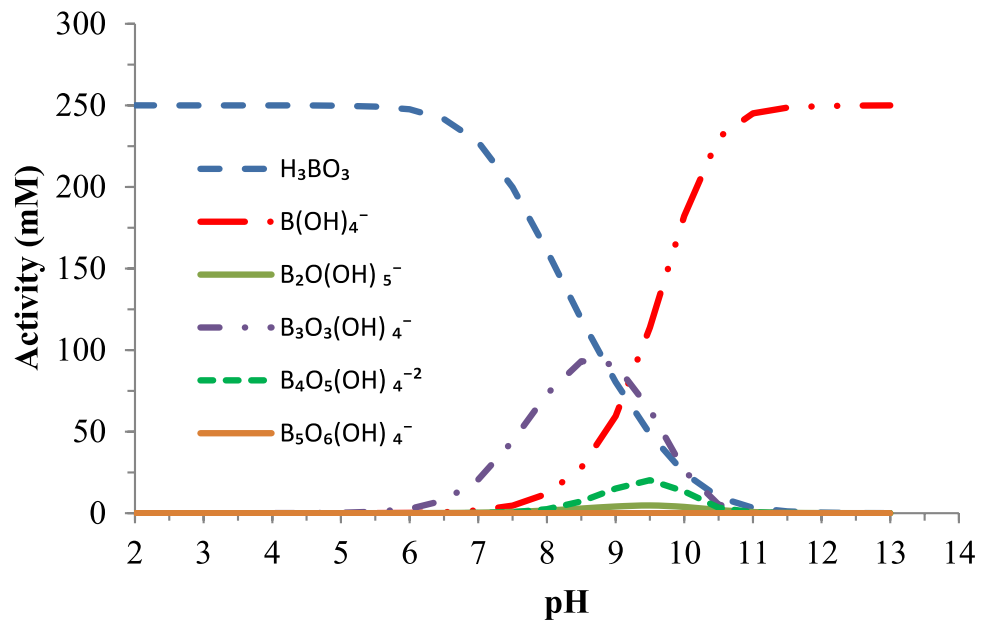


Fig. 4 Dissolution changes of calcium ions at changing pH for synthetic solutions

increases with temperature increase, but the removal percentage for exothermic processes decreases with temperature increase (Öztürk and Köse 2008; Korkmaz et al. 2016). The parameters for temperature effect were pH 5.32–5.47, stirring speed 300 rpm, dosage 15 g/L, concentration 2541 mg/L and wastewater volume 500 mL. Boron removal results are given in Fig. 5A and operation pH are given in Fig. 5B. The temperature increase decreased the dissolution of calcium hydroxide to a small degree and more calcium hydroxide existed in the solution and more boron removal was expected to occur at high temperature. However, removal performance of calcium hydroxide increased with decreasing temperature. The exothermic nature of the removal eliminated the extra effect of calcium hydroxide on removal at high temperature.

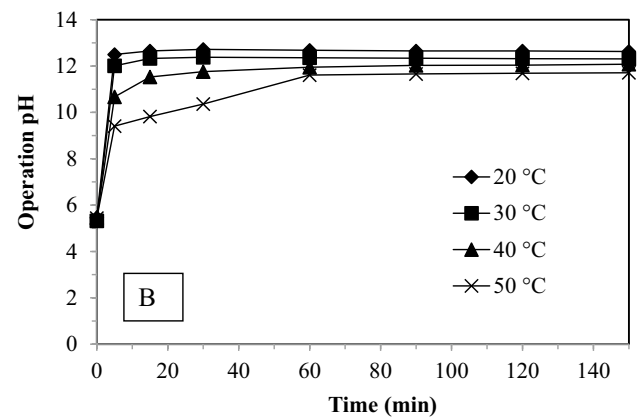
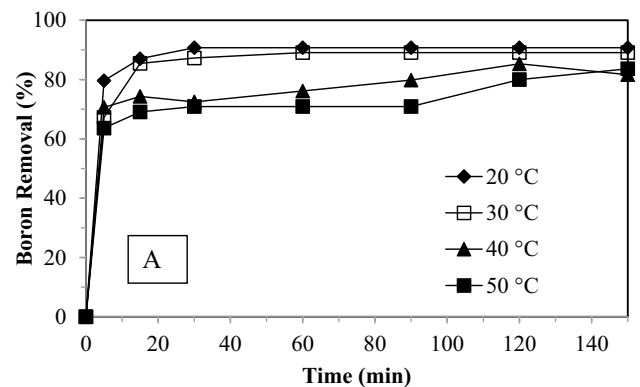


Fig. 5 **A** Temperature effect on boron removal by calcium hydroxide (calcium hydroxide amount 15 g/L, 300 rpm, pH 5.38–5.47, 500 mL wastewater volume). **B** Operation pH change during removal

The end point operation pH for 20, 30, 40 and 50 °C were 12.63, 12.31, 12.08 and 11.71. pH change of solutions was due to the dissolution of calcium hydroxide. The process indicates that the exothermic process and low temperature supported the adsorption of boron on calcium hydroxide at near adsorption of sulphate and total arsenic (III). Boron removal for 20, 30, 40 and 50 °C temperatures are 90.74, 89.09, 81.65 and 83.63%. In a study, boron removal by sub-micron calcium hydroxide produced from calcium chloride and calcium nitrate tetrahydrate was reported as optimum at 95 °C (Tsai and Lo 2015). It was thought that the reason for this high temperature which is different from the present study was the purity of the boron solution from sulphate because the sulphate adsorption is high at high temperature for the present study and sulphate strongly decreases the boron removal by calcium hydroxide (Tsai and Lo 2011). On the other hand, in another study, boron removal was the same from 50 to 70 °C and increased at 90 °C for experimental conditions of 0.7 g/L boron concentration, 45 g/L calcium hydroxide amount, 450 rpm stirring speed, 50 g/L sulphuric acid and 2 L synthetic solution volume (Remy et al. 2005). The optimum high temperature (90 °C) was due to the probably formed strong calcium sulphate (gypsum) that enables the adsorption of boron at high temperature (Remy et al. 2005). This is because the sulphate adsorption on calcium hydroxide at low temperature is poor. The low optimum temperature in the present study is quite economical for boron removal due to high energy consumption for heating of the wastewater. In the present study, there is no formation of gypsum-adsorbing boron; only sulphate was adsorbed physically.

Effect of Ca(OH)₂ amount on boron removal

The effect of calcium hydroxide amount was studied between 10 and 25 g/L, and other parameters were pH 5.32–5.64, stirring speed 300 rpm, temperature 30 °C, concentration 2541 mg/L and wastewater volume 500 mL. The results are given in Fig. 6A and operation pH are given in Fig. 6B. As can be seen in Fig. 6A, the boron removal from 5 to 7.5 g/500 mL calcium hydroxide amounts increased up to about 89.09% removal percentage, and thereafter the removal attained a plateau. The increase of pollutant removal percent with adsorbent or coagulant increase is generally the normal trend as the active sites of the materials increase with dosage increase. This plateau trend was considered to be related with mass balance between boron and calcium hydroxide (Korkmaz et al. 2016; Avila et al. 2021). In the literature, boron adsorption onto calcinated alunite and Dowex 2 × 8 resin showed a similar trend exhibiting the plateau for increasing adsorbent dosage (Öztürk and Köse 2008; Kavak 2009). Operation pH for 5, 6, 7.5, 10 and 12.5 g/500 mL dosages were 10.5, 12.05,

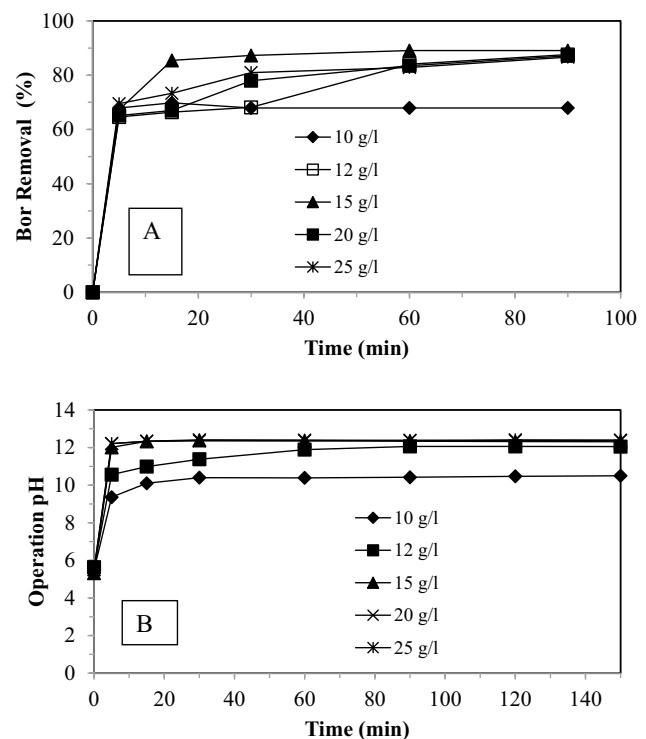


Fig. 6 **A** Calcium hydroxide effect on boron removal (30 °C, 300 rpm, pH 5.38–5.64, 500 mL wastewater volume). **B** Operation pH change during removal

12.31, 12.37 and 12.40, and the dissolution of calcium hydroxide can be neglected. Boron removal percentages are 69.81, 85.84, 89.09, 88.99 and 88.57% for 5, 6, 7.5, 10 and 12.5 g/500 mL calcium hydroxide amounts. While boric acid, monoborate and polyborates were present at 5 g calcium hydroxide amount, there were only boric acid and monoborate in the wastewater at calcium hydroxide amount range between 6 and 12.5 g. In several studies, boron removal percentages became stable at high calcium hydroxide amounts, and this result was due to the solid-to-solution ratios (Remy et al. 2005; Tsai and Lo 2015; Akkurt et al. 2022; Yu et al. 2022). The boron adsorption onto calcium hydroxide was determined as concentration dependent, and boron adsorption was influenced by boron-to-calcium hydroxide amount ratio. Therefore, boron adsorption was constant at high calcium hydroxide amounts. Also, high operation pH at high calcium hydroxide amounts can cause constant removal efficiency due to stripping effect of hydroxyl ions at high pH.

Effect of stirring speed on boron removal

The effect of stirring speed is an important parameter to decrease the liquid film resistance surrounding the adsorbent and to increase the opportunity of pollutant–adsorbent

interaction in the reactor body (Fil et al. 2012; Korkmaz et al. 2016). The studied parameters for boron removal by calcium hydroxide were pH 5.32–5.42, temperature 30 °C, dosage 15 g/L, wastewater volume 500 mL and stirring speed 150–375 rpm. The results are given in Fig. 7A and operation pHs are given in Fig. 7B. The stirring speed was ineffective for boron removal at equilibrium conditions, but the speed of removal or the rate of adsorption increased with increasing stirring speed at beginning reaction times. The increase of adsorption rate by increasing stirring speed was due to the decreasing liquid film resistance or rising of speed of opportunity of interaction between boron and calcium hydroxide (Fil et al. 2012; Korkmaz et al. 2016). The removal percentages are 86.92, 88.99, 89.09 and 87.39% for 150, 225, 300 and 375 rpm, respectively. Similarly, boron removal by selective Purolite S 108 resin did not significantly change in a batch reactor at different stirring speeds (Korkmaz et al. 2016). Also, it was reported that dye removal by sepiolite clay was not affected by changing stirring speeds (Doğan et al. 2007). In another selective boron removal by ion exchange, the stirring speeds from 350 to 550 rpm did not influence the removal (Mohammed et al. 2014). The change of operation pHs by increasing stirring speeds were the same; therefore, stirring speed is not effective for dissolution of calcium hydroxide. The studied stirring speeds changing from 150 to 375 rpm were effective

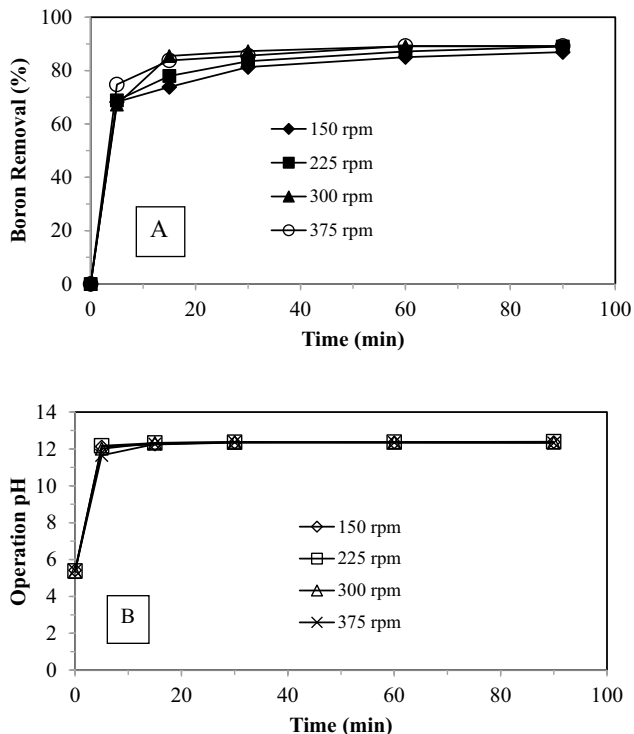


Fig. 7 **A** Stirring speed effect on boron removal by calcium hydroxide (calcium hydroxide amount 15 g/L, 30 °C, pH 5.3–5.4, 500 mL wastewater volume). **B** Operation pH change during removal

on initial boron removal rate and increased the initial boron removal rate from 150 to 375 rpm stirring speeds at beginning reaction times. The stirring speed values were adequate and therefore there is no necessity to increase extra stirring speed. This is because the boron adsorption percentages on the calcium hydroxide did not change by increasing stirring speeds.

Kinetic analysis of boron removal

The kinetic analysis of removal of boron by calcium hydroxide provides the determination of optimum time and design of batch reactor and degree of adsorption kinetic model. The general kinetic models for adsorption of pollutants include pseudo-first-order, pseudo-second-order, elemental kinetic model, Elovich model and modified Freundlich model, but these models are based on adsorption capacities (Korkmaz et al. 2017). Therefore, the zero-order, first-order and second-order models which are not based on adsorption capacity are preferred for analysis. Since the adsorbent amounts of calcium hydroxide in the study are changed based on time, the pH of the solutions change and therefore adsorption capacities cannot be calculated. The fitness of the kinetic models were interpreted based on parameters and their values. The rate constants were also interpreted. The zero-order, first-order and second-order models are mathematical models and therefore there is no assumption for their development. Only the second-order model shows the concentration dependence of removal due to second-degree dependence of the model to the concentration. The kinetic models used for analysis of boron removal are zero-order, first-order and second-order kinetic models that are derived from the following differential equation (Yılmaz 2009; Korkmaz 2023; Mohammed et al. 2023):

$$\left(\frac{dC}{dt} = -kC^n\right) \quad (3)$$

The zero-order kinetic model is as follows:

$$C = C_0 - kt \quad (4)$$

The first-order kinetic model is as follows:

$$\ln(C) = \ln(C_0) - kt \quad (5)$$

The second-order kinetic model is as follows:

$$\frac{1}{C} = \frac{1}{C_0} - kt \quad (6)$$

Here, C_0 is the initial boron concentration (mg/L), C (mg/L) is the boron concentration at time t (min) and k is the rate constant (min^{-1}).

The kinetic analysis results are given in Table 2. As can be seen in Table 2, boron removal kinetic data fitted

Table 2 Kinetic analysis of boron removal

Parameters				Zero order $C_t = C_0 - k_t$		First order $\ln(C_t) = \ln(C_0) - k_t$		Second order $1/C_t = 1/C_0 + kt$	
pH	Temperature (°C)	Ca(OH) ₂ (g/L)	Stirring speed(rpm)	k_0	R^2	k_1	R^2	$k_2 \times 10^6$	R^2
1.00	30	15	300	5.147	0.804	0.006	0.849	-7	0.89
2.50	30	15	300	5.454	0.885	0.014	0.983	-30	0.999
4.00	30	15	300	3.374	0.650	0.008	0.768	-20	0.875
5.32	30	15	300	8.074	0.534	0.016	0.627	-40	0.741
7.00	30	15	300	3.906	0.807	0.006	0.89	-10	0.954
8.50	30	15	300	8.430	0.907	0.011	0.943	-20	0.963
5.42	30	15	150	4.045	0.817	0.008	0.905	-20	0.967
5.38	30	15	225	5.3	0.777	0.011	0.882	-30	0.957
5.40	30	15	375	3.647	0.671	0.013	0.854	-30	0.934
5.46	20	15	300	10.92	0.909	0.03	0.960	-90	0.992
5.47	40	15	300	2.921	0.929	0.005	0.906	-10	0.866
5.44	50	15	300	2.997	0.857	0.004	0.850	-8	0.825
5.50	30	10	300	-0.245	0.013	-0.000	0.013	0.4	0.013
5.64	30	12	300	7.395	0.940	0.013	0.949	-30	0.953
5.52	30	20	300	4.077	0.806	0.008	0.888	-20	0.948
5.50	30	25	300	3.979	0.867	0.008	0.938	-20	0.977

Bold shows fitness

to the second-order model with a coefficient of determination value of 0.013–0.999. The fitness of data to the second-order model showed the concentration-dependent adsorption of boron onto calcium hydroxide. The adsorption rate constants for the second-order model increased at moderate pHs (5.32), high stirring speeds (300 rpm), low temperatures (20 °C) and moderate solid amounts (7.5 g). According to second-order rate constants of temperature (Table 2), boron adsorption rates decreased with increasing solution temperatures. However, the viscosity of the wastewaters decreased with high temperature. The negative value of second-order model rate constant shows only decreasing trend of the concentration, and it is due to nature of the model. In the removal of boron, sulphate and arsenic by calcium hydroxide, precipitation, ion exchange and adsorption mechanism together played a role. These are probably ion exchange between hydrogen ions of calcium hydroxide and boron ions, surface adsorption and co-precipitation (Itakura et al. 2005). However, there are no chemical formations between calcium hydroxide and pollutants at 20 °C, which is the optimum temperature.

Thermodynamic parameters of boron removal

The activation energy is the required external energy that should be given to a reaction medium for starting the

reaction. The activation energy of boron removal was calculated from the Arrhenius equation (Doğan et al. 2007; Korkmaz et al. 2016).

$$\ln(k) = \ln k_0 - \frac{E_a}{RT} \quad (7)$$

Here, E_a is the activation energy of boron adsorption (kJ/mol), k is the second-order rate constant of removal (min^{-1}), k_0 is Arrhenius factor, R is the ideal gas constant (J/K mol) and T is the solution temperature (K). The thermodynamic analysis of adsorption data based on temperature provides information about the nature of the adsorption process (i.e. physical or chemical reaction or spontaneous or unspontaneous) (Elass et al. 2011). The enthalpy change and entropy change of boron removal are related with the following equation (Eyring 1935; Doğan et al. 2007; Korkmaz et al. 2020a):

$$\ln\left(\frac{k}{T}\right) = \left[\left(\frac{k_B}{h}\right) + \frac{\Delta S}{R}\right] - \frac{\Delta H}{RT} \quad (8)$$

where k_B and h are Boltzmann's ($1.3807 \times 10^{-16} \text{ cm}^2 \text{ gs}^{-2} \text{ K}^{-1}$) and Planck's constants ($6.6261 \times 10^{-27} \text{ cm}^2 \text{ gs}^{-1}$), respectively. ΔH (enthalpy change) and ΔS (entropy change) were calculated from slope and intercept of the linear line, respectively (Korkmaz et al. 2020a). k is the second-order reaction rate constant and R is the gas constant (8.314 J/mol K).

The enthalpy value of boron adsorption was calculated as -70.9 kJ/mol , and this value showed the exothermic

nature of the boron adsorption with calcium hydroxide (Elass et al. 2011). The entropy of the system was calculated as 1.73×10^{11} showing the increasing randomness of adsorption (Elass et al. 2011). The activation energy of the system was calculated as 7.2 J/mol. This indicates that the system requires external interaction energy for starting the reaction (Korkmaz et al. 2016). A negative ΔH value indicates that the pollutant removal increases at low temperature and boron removal increases at low temperature. Also, a positive ΔS value indicates the increasing randomness at solid–solution interface with temperature increase. The boron removal was found to be physical and this can indicate the high desorption probability at solid–solution interface at high temperatures. The decreasing or low enthalpy values show physical adsorption. The low activation energy also supported the physical adsorption.

Adsorption mechanisms are mostly categorised into physisorption and chemisorption. Physisorption has weak van der Waals forces, which would lead to low adsorption enthalpies, which are between 5 and 40 kJ/mol. The process is generally reversible and happens at very low temperatures, and it could also occur between multiple layers on the adsorbent material. On the other hand, the process of chemisorption is based on the formation of strong chemical bonds between the adsorbate and the surface, and these are known to have higher enthalpies ranging between 40 and 800 kJ/mol. Chemisorption is also irreversible, and these are favoured at higher temperatures, which also require higher activation energy (Ahmed Alsharif, 2025).

Diffusion mechanism analysis of boron removal

Also, it was investigated which step was controlling diffusion of boron into calcium hydroxide. Assuming adsorption of boron into the calcium hydroxide as a liquid–solid phase reaction, which includes diffusion of boron from liquid phase to the calcium hydroxide surface and the diffusion of ions within the calcium hydroxide pores, two possible diffusion mechanisms can be proposed (Alguacil et al. 2004; Korkmaz et al. 2016).

Film and particle diffusion models for the infinite solution volume conditions were described by the following equations. The following diffusion kinetic models indicate stable (adsorption). At the same time, in these models, all adsorbent particles are assumed as spherical and uniformly sized (Luque 1982; Korkmaz 2023). The diffusion models below have been widely applied in ion-exchange systems (Luque 1982; Alguacil et al. 2004; Korkmaz et al. 2016).

A fractional approach to the equilibrium:

$$X_B = [(C_0 - C_t)/(C_0 - C_e)] \quad (9)$$

Film diffusion–controlled process:

$$\ln(1 - X_B) = -k_f t \quad (10)$$

Particle diffusion–controlled process:

$$\ln(1 - X_B^2) = -k_p t \quad (11)$$

where X_B is the fractional approach to the equilibrium, k_f is the film diffusion rate constant and k_p is the particle diffusion rate constant.

Diffusion models for unreacted nuclei in constant size spherical particles were analysed by the following equations. In this type of reactions, the reaction is generally heterogeneous and it is assumed that the size of the solid particle does not change due to the unchanged ash layer in thickness during the reaction (Temur et al. 2000; Kurtbas et al. (2006); Korkmaz 2023).

Film diffusion–controlled process:

$$(X_B) = k_f t \quad (12)$$

Ash layer–controlled process

$$1 - 3(1 - X_B)^{2/3} + 2(1 - X_B) = k_{ash} t \quad (13)$$

Chemical reaction–controlled process:

$$(1 - (1 - X_B)^{1/3}) = k_{chem} t \quad (14)$$

where X_B is the fractional approach to the equilibrium, k_f is the film diffusion rate constant, k_{ash} is the ash film diffusion rate constant and k_{chem} is the chemical reaction–controlled process rate constant.

The analysed diffusion models showed that the rate-controlling mechanisms are particle diffusion and chemical reaction when the two approaches of the analyses were taken into consideration. Diffusion analysis results are given in Tables 3 and 4. The particle diffusion and chemical reaction limitation for the reaction showed that the slow chemical reaction on the calcium hydroxide surface and insufficient size of pores of calcium hydroxide controlled the adsorption rate. Also, the chemical reactions on the calcium hydroxide surface and its pores controlled the removal of boron. The unimportant effect of stirring speed on the rate also indicated low effect of liquid film layer. The molecular size of boric acid is several hundred picometers, and the size of polyborates is higher than it. The average pore size of calcium hydroxide was measured as 1339.6 nm. Also, during the adsorption, calcium hydroxide particles might be broken down to give small particles and pore dimension might be smaller by this breakdown and smaller calcium hydroxide particles might block the high-dimensional pores (Tsai and Lo 2015). This probably concluded in pore and chemical reaction limitations because each pore and small particles in the blocked pores have their own diffuse layer resulting in pore and

chemical reaction limitation (Korkmaz 2023; Yükselen and Kaya 2003). Also, the formed $\text{Ca}(\text{OH})^+$ ions and wastewater magnesium ions might cause the attachment of small particles to the pore mouth of big particles. The natural narrow pore size of calcium hydroxide also might cause the pore diffusion and chemical reaction–controlled process. The SEM figures of raw calcium hydroxide and treated calcium hydroxide are given in Fig. 8. The calcium hydroxide particles were assumed as spherical and to have uniform size for boron adsorption in the analysis of the diffusion models (infinite solution volume models). Also, the SEM images of the raw calcium hydroxide is shown in the text to see the shape of particles. The particle size fraction of calcium hydroxide was measured by sieve analysis during 15 min as > 1.44 mm (2.84%), 850 μm to 1.4 mm (19.15%), 600–850 μm (3.17%) and < 600 μm (74.84%), and its pore size was assumed as small at small particle sizes. Also, particle diffusion–controlled process behaviour can be expected for calcium hydroxide with small particle size as the small particles would have low pore size. Due to the different particle sizes of calcium hydroxide, in the analysis of particle diffusion models for infinite solution volume approach, it became to be calculated as the ‘average diffusion rate constants’ from short particle size to long particle size. There are two main particle size groups (< 600 μm and 850 μm to 1.4 mm). From the SEM images of the raw calcium hydroxide, while some particles are so near spherical size, some particles are trapezoid (Fig. 8). Also, the general physical trend of boron adsorption could be controlled by a chemical

reaction–controlled process, and this can be due to weak hydrogen exchange reactions between boron and calcium hydroxide particles and $\text{Ca}(\text{OH})^+$ molecules (Itakura et al. 2005). For these reasons, in the analysis of film and particle diffusion model for infinite solution volume conditions, the ‘average diffusion rate constants’ could be calculated due to two different particle size fractions. The particle diffusion rate constants were below film diffusion rate constants due to particle diffusion fitness to the data in infinite solution volume approach. Although the chemical–controlled process fitted to the data rather than film and ash layer–controlled process in constant size spherical particle approach, the rate constants of these three models showed disharmony with respect to rate constants. This situation may be due to the nature of the equations or the closeness of the correlation coefficients (R^2) with each other. The shrinkage of calcium hydroxide was low due to low dissolution for fitness to unreacted nuclei in constant size model.

Central composite experimental design of boron, sulphate and total arsenic (III) removal

The treatment processes sometimes require optimisation of the removal data for maximum output. In the literature, there are several techniques for optimisation such as response surface methodology, two or more levelled factorial design, Taguchi, artificial neural network and traditional one-parameter experimental optimisation technique (Doğan 2007); Çalgan 2023; Korkmaz 2023; Süzen 2023).

Table 3 Diffusion analysis of boron removal (for infinitive solution volume model) (wastewater volume is 500 mL)

Parameters				Film diffusion $\ln(1 - X_B) = -kt$		Particle diffusion $\ln(1 - X_B^2) = -kt$	
pH	Temperature (°C)	$\text{Ca}(\text{OH})_2$ (g/L)	Stirring speed (rpm)	R^2	k	R^2	k
1.00	30	15	300	0.764	0.0854	0.834	0.0686
2.50	30	15	300	0.861	0.2898	0.847	0.2824
4.00	30	15	300	0.825	0.1167	0.881	0.0955
5.32	30	15	300	0.879	0.1249	0.913	0.1069
7.00	30	15	300	0.877	0.0263	0.937	0.0231
8.5	30	15	300	0.951	0.0563	0.968	0.0484
5.42	30	15	150	0.855	0.6005	0.839	0.5833
5.38	30	15	225	0.860	0.0558	0.931	0.0484
5.40	30	15	375	0.824	0.1169	0.880	0.0998
5.46	20	15	300	0.869	0.1985	0.921	0.1594
5.47	40	15	300	0.670	0.0298	0.752	0.0249
5.44	50	15	300	0.628	0.016	0.697	0.0132
5.5	30	10	300	0.035	−0.0516	0.035	−0.0419
5.64	30	12	300	0.873	0.0541	0.894	0.0468
5.52	30	20	300	0.886	0.0294	0.934	0.0261
5.50	30	25	300	0.823	0.0334	0.898	0.0291

Bold shows fitness

Table 4 Diffusion analysis of boron removal (for fixed size particle model) (wastewater volume is 500 mL)

Parameter			Film Diffusion		Ash Layer Diffusion			Chemical Reaction	
pH	Temp. (°C)	Ca(OH) ₂ (g/l)	$t = \frac{\rho B \times r}{3bk_s C_{Ag}} (X_B)$		$1 - 3(1 - X_B)^{2/3} + 2(1 - X_B) = \frac{\rho B \times r^2}{D_{ex} \times C_{Ag} \times 6b} t$			$(1 - (1 - X_B)^{1/3}) = \frac{\rho B \times r}{b \times k_s \times C_{Ag}} \times t$	
			Stir. Speed(rpm)	R ²	k	R ²	k	R ²	k
1,00	30	15	300	0,804	0.003	0,832	0.0316	0,970	0.0102
2,50	30	15	300	0,885	0.0024	0,993	0.0311	0,990	0.0105
4,00	30	15	300	0,631	0.0011	0,816	0.0324	0,946	0.0072
5,32	30	15	300	0,534	0.035	0,634	0.0245	0,913	0.0102
7,00	30	15	300	0,807	0.0018	0,879	0.0119	0,934	0.0039
8,50	30	15	300	0,907	0.0041	0,996	0.034	0,993	0.0084
5,42	30	15	150	0,817	0.0019	0,917	0.0219	0,986	0.0074
5,38	30	15	225	0,777	0.0023	0,866	0.0218	0,977	0.0067
5,40	30	15	375	0,753	0.0025	0,816	0.0321	0,966	0.0141
5,46	20	15	300	0,909	0.0047	0,968	0.0386	0,989	0.02
5,47	40	15	300	0,929	0.0013	0,876	0.0068	0,748	0.004
5,44	50	15	300	0,857	0.0014	0,849	0.0093	0,737	0.0033
5,5	30	10	300	0,594	0.0578	0,013	0.0038	0,013	-0.0024
5,64	30	12	300	0,940	0.0034	0,910	0.0244	0,936	0.0077
5,52	30	20	300	0,806	0.0018	0,931	0.0184	0,947	0.0041
5,50	30	25	300	0,867	0.0017	0,901	0.0136	0,936	0.0047

Bold shows fitness

The central composite design tool of response surface optimisation method for boron, total arsenic (III) and sulphate removal from boric acid plant wastewater was applied. The central composite design was applied for optimisation with a total of 15 experimental runs. For central composite design, the Minitab 16.0 program was used. Central composite design consists of 2^k factorial points (also called cube points), where k is the number of factors (Kasina et al. 2020; Korkmaz 2023). A central composite design matrix with two factors is shown in Fig. 9. Points on the diagrams represent the experimental runs that are performed (Çalgan 2023; Süzen 2023). The factorial and centre points may serve as a preliminary stage for central composite design (Kasina et al. 2020). Anyone can then build up the factorial design into a central composite design to fit a second-degree model by adding axial and centre points. Central composite designs allow for efficient estimation of the quadratic terms in the second-order model (Korkmaz 2023). The regression model should be arranged by equations, namely linear, linear plus squares, linear plus interaction and full quadratic approaches. The low and high values of experimental parameters are given in Table 5. The analyses for linear, linear plus squares, linear plus interaction and full quadratic equation approaches are given in Table 6. The experimental matrixes for boron, sulphate, total arsenic (III) and removal responses are given in Table 7. ANOVA is given in Table 8. The experimental parameters for matrix were selected from boron

kinetic experiments as pH 1–9, dosage 5–25 g/L, stirring speed 300 rpm, wastewater volume 500 mL, operation time 150 min and temperature 20–60 °C. The time for removal of contaminants was selected as 150 min, and this was enough for these three contaminants from preliminary experiments. The confidence level for optimisation was selected by the program as 95% (p < 0.05). The response for the statistical analysis was the boron, sulphate and total arsenic (III) removal percentages. The p values (probability constants) were used as a control parameter to check the reliability of the developed statistical model, individual and interaction effects of the parameters (Montgomery 1991; Kavak 2009, 2011). In general, the larger the magnitude of t and the smaller the value of p, the more significant is the corresponding coefficient term (Montgomery 1991; Kavak 2009, 2011). The general regression model is given as follows:

$$\begin{aligned} \% (Removal) = & b + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_1X_1 + b_5X_2X_2 + b_6X_3X_3 \\ & + b_7X_1X_2 + b_8X_1X_3 + b_{10}X_2X_3 + b_{11}X_1X_2X_3 + \epsilon \end{aligned} \tag{15}$$

Here, the b parameters (b, b₁, b₂, ... b_n) are model constants. The X terms (X₁, X₂, ... X_n) are the coded factors. The analysis was done based on uncoded parameter values (i.e. real parameter values).

The regression analysis for boron showed that all the parameters were statistically unimportant. We think that the statistically unimportant or meaningless results occur in the case of

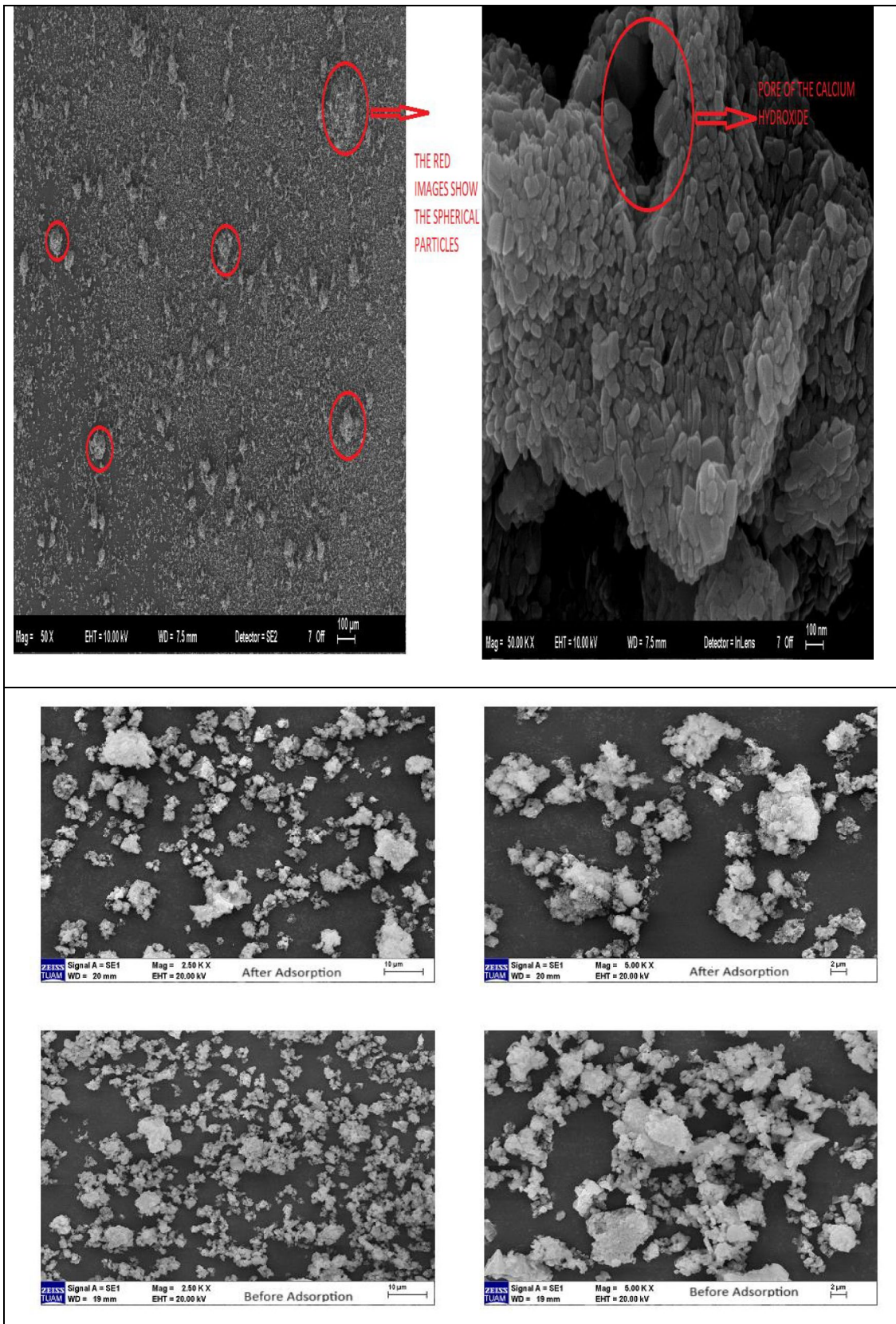
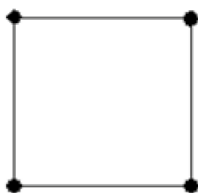
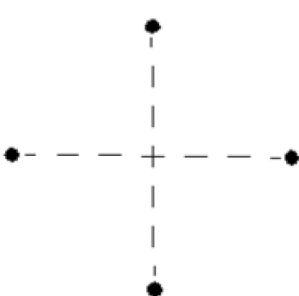


Fig. 8 SEM images of calcium hydroxide before and after removal (20 °C, 20 g Ca(OH)₂/500 mL, 200 rpm, 150 min and pH 5.88)

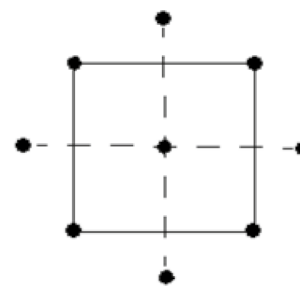
Fig. 9 The experimental matrix space for boron, sulphate and total arsenic (III) removal



The points in the factorial portion of the design are coded to be -1 and +1.



The points in the axial (star) portion of the design are at: (+2, 0), (-2, 0), (0, +2), (0, -2)



Here, the factorial and axial portions along with the center point are shown. The design center is at (0,0).

narrow effect of parameter change from low value to high value on response. The general regression model is as follows.

$$\begin{aligned} (\%) \text{ Boron Removal} = & 72.004 - 0.6203pH + 14.0524S - 2.5532T - 8.3938pH * pH \\ & - 6.6713S * S + 6.0535T * T + 4.4088pH * S - 2.6708pH * T - 2.7346S * T \end{aligned}$$

It was reported for sulphate removal that all the parameters were statistically unimportant. The general regression model is as follows:

$$\begin{aligned} (\%) \text{ Sulphate Removal} = & 31.2633 - 8.4073pH - 2.2084S + 0.9440T - 10.5968pH * pH \\ & - 3.6397S * S - 19.6884T * T - 13.2469pH * S - 9.4101pH * T + 11.7834S * T \end{aligned}$$

The important factors for arsenic removal were reported by the program as model constant, solid and solid–solid interaction. The general regression model is given as follows:

$$\begin{aligned} (\%) \text{ Total Arsenic (III) Removal} = & 103.327 + 0.650pH + 5.758S + 1.875T - 1.663pH * pH \\ & - 17.555S * S - 3.911T * T - 2.762pH * S - 2.766pH * T - 2.844S * T \end{aligned}$$

Here, pH is solution pH, *T* is temperature (°C) and *S* is solid amount (g/500 mL).

The surface plots are given in Figs. 10, 11 and 12. As can be seen in Fig. 10, boron removal increased at

moderate pH and high adsorbent amount interaction. Sulphate removal increased at moderate pH and moderate adsorbent amount interaction. Arsenic removal increased at moderate adsorbent amount and high pH interaction. It is clear from Fig. 11 that boron removal increased at moderate pH and minimum and maximum temperature interactions. Sulphate removal increased at moderate pH and moderate temperature interaction. Arsenic removal increased at moderate pH and moderate temperature interaction. In Fig. 12, boron removal increased at high adsorbent amount and constant temperature interaction. Sulphate removal increased at high adsorbent amount

Table 5 The low and high values of parameters

Parameter and levels	-2	-1	0	1	2
pH	1	3	5	7	9
Temperature (°C)	20	30	40	50	60
Calcium hydroxide (g/500 mL)	2.5	5	7.5	10	12.5

Table 6 Analysis of matrix data with respect to coefficient of determination values for different model equations

Model equation	R-Sq (%)	R-Sq (adjusted) (%)
Linear		
Boron	57.61	46.04
Sulphate	6.61	0.00
Total arsenic (III)	23.25	2.32
Linear + square		
Boron	75.73	57.53
Sulphate	23.15	0.00
Total arsenic (III)	78.0	61.49
Linear + interaction		
Boron	58.81	27.91
Sulphate	18.08	0.00
Total arsenic (III)	25.09	0.00
Full quadratic		
Boron	76.93	35.40
Sulphate	34.61	0.00
Total arsenic (III)	79.83	43.52

and moderate temperature interaction. Arsenic removal increased at moderate adsorbent amount and moderate temperature interaction. According to the study of Yu et al., sulphate removal by calcium hydroxide decreased below initial pH of 3 and constant between 4 and 9 and sulphate removal was not affected by dosage increase. In

the same study, sulphate removal decreased below 30 °C temperature, and the temperature from 30 to 75 °C did not affect the sulphate removal (Yu et al. 2018). The sulphate removal showed similarities at 20 °C with that in Yu et al.’s study, and while the removal of sulphate was a bit high above 20 °C in that study, its removal was 0% for 20 °C, 15 g/L and pH 5 in the present study. This non-adsorption of sulphate can be related to the boron, arsenic and sulphate competitive adsorption on calcium hydroxide and low-temperature effect. The R-Sq values for boron, sulphate and total arsenic (III) were obtained from the Minitab 16.0 software as 76.93%, 34.61% and 79.83%. It is well known that R-Sq value above 75% was assumed as satisfactory for estimation of the data by the models. Therefore, while the developed full quadratic models for boron and total arsenic (III) are satisfactory, the error for sulphate seems as high. The maximum errors for estimation of developed models to the real removal data are 8.60% for boron, 19.10% for sulphate and 1.7% for total arsenic (III). Therefore, although the R-Sq values of full quadratic model for sulphate removal was around moderate descriptive, the optimisation Figs. 10, 11 and 12 gave the optimum parameter trends as satisfactory for the sulphate removal. The trends of sulphate removal in Figs. 10, 11 and 12 were confirmed by the study of Yu et al. (2018). This low R-Sq and important statistical results conditions have been faced sometimes by the researchers and the description of such conditions would be important for science. There was no choice for change of parameters or

Table 7 Experimental matrix for boron, sulphate and boron removal

Run	Parameters			Response			Estimation		
	pH	Ca(OH) ₂ (g/500 mL)	Temperature (°C)	Boron (%)	Sulphate (%)	Total arsenic (III) (%)	Boron (%)	Sulphate (%)	Total arsenic (III) (%)
1	3	5	30	66.37	32.03	98.39	64.04	22.19	97.59
2	7	5	30	66.37	43.84	99.93	62.54	30.15	98.54
3	3	10	30	69.91	38.69	100.00	77.25	21.49	99.98
4	7	10	30	76.99	9.93	99.95	80.17	13.14	100.00
5	3	5	50	66.98	41.81	100.00	64.14	22.71	98.95
6	7	5	50	66.98	16.89	99.95	59.97	18.20	99.12
7	3	10	50	70.45	39.04	100.00	74.62	36.84	100.00
8	7	10	50	72.19	22.09	100.00	74.87	16.04	99.94
9	1	7.5	40	67.27	6.32	100.00	64.19	22.54	100.00
10	9	7.5	40	60.38	10.03	100.00	62.94	9.69	100.00
11	5	2.5	40	43.16	17.31	92.75	51.23	30.01	94.45
12	5	12.5	40	87.94	23.95	98.36	79.34	27.14	97.66
13	5	7.5	20	82.62	0.00	98.74	80.60	10.82	99.32
14	5	7.5	60	73.93	9.16	100.00	75.40	14.23	100.00
15	5	7.5	40	72.44	17.27	100.00	71.96	33.16	100.00

Table 8 ANOVA of boron, sulphate and arsenic removal

Term	Boron			Sulphate			Total arsenic (III)		
	Constant	T	P	Constant	T	P	Constant	T	P
Constant	46.2799	0.584	0.584	-96.7763	-0.517	0.627	75.3177	5.423	0.003
pH	4.7731	0.506	0.635	21.3903	0.959	0.382	1.0129	0.612	0.567
D	6.8049	0.852	0.433	0.6052	0.032	0.976	3.7796	2.697	0.043
T	-0.9663	-0.429	0.686	3.8792	0.729	0.499	0.3530	0.894	0.412
pH-pH	-0.5246	-0.863	0.428	-1.0653	-0.742	0.492	-0.0291	-0.273	0.796
D-D	-0.2669	-0.686	0.523	-0.1836	-0.20	0.850	-0.1964	-2.879	0.035
T-T	0.0151	0.622	0.561	-0.0516	-0.898	0.410	-0.0027	-0.641	0.550
pH-D	0.2204	0.385	0.716	-0.8149	-0.603	0.573	-0.0386	-0.385	0.716
pH-T	-0.0334	-0.233	0.825	-0.1558	-0.461	0.664	-0.0097	-0.386	0.716
D-T	-0.0273	-0.239	0.821	0.1484	0.549	0.607	-0.0080	-0.396	0.708

Constant: model constant, T: Student test, P: confidence constant (95% $p < 0.05$),
pH: pH, D: dosage (g/500 mL), T: temperature ($^{\circ}\text{C}$)

levels for improvement of R-Sq value of sulphate because there are three different responses and limited parameters such as temperature, pH and calcium hydroxide amount.

On the other hand, there is no necessity to estimate sulphate removal by the model because sulphate removal was low. Therefore, sulphate removal needs an advanced removal such as ion exchange. The regression model was established using ANOVA. The estimation of the developed regression models to the data is given in Table 7, and the estimation of the data by the models was better for boron and arsenic than sulphate. The developed regression model for boron and arsenic demonstrates confidence, but its reliability for sulphate is low and its estimation of sulphate removal trend for the parameters is strong with respect to surface graph coverage. The sulphate surface graphs could estimate the data trends well using regression model by the program. It was difficult to obtain high regression R-Sq values in the analysis because there are three experimental parameters and three responses. It is well known that R-Sq value above 75% was assumed as satisfactory for estimation of the data by the models.

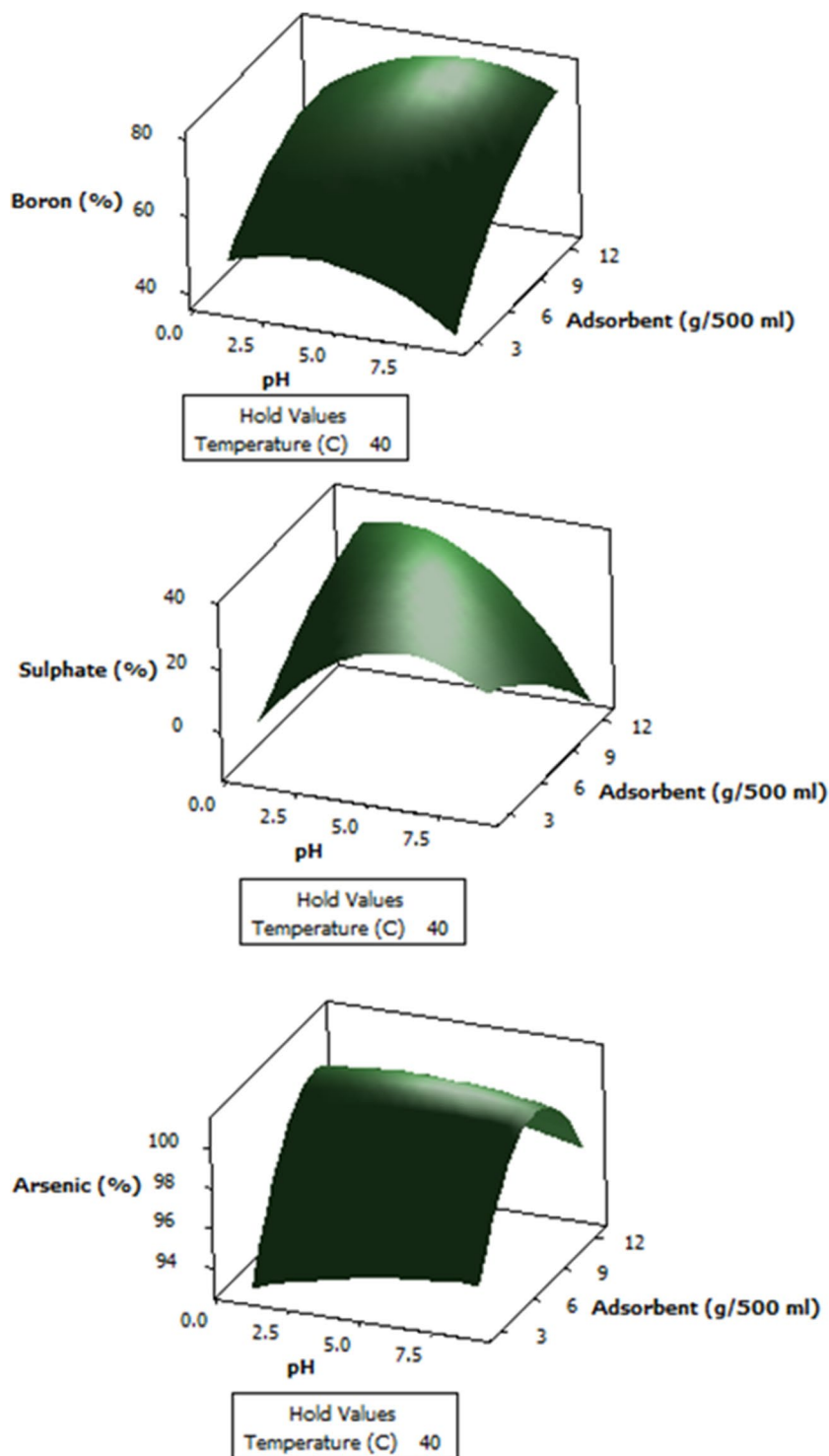
In the study of Remy and coworkers, the presence of sulphate in boron solution was reported to be inhibitive of the boron removal yield by calcium hydroxide from 50 to 70 $^{\circ}\text{C}$ and the boron removal increased at 90 $^{\circ}\text{C}$ due to probably the formation of calcium sulphate (Remy et al. 2005). In the present study, boron removal at 20 $^{\circ}\text{C}$ was high from 50 $^{\circ}\text{C}$ due to low or no sulphate adsorption providing more adsorption site for boron. In the study of Tsai and coworkers, boron removal by calcium hydroxide decreased in the presence of sulphate from 0 to 500 mg/L sulphate concentration (Tsai and Lo 2011). In the mentioned study, constant phosphoric acid amount was used as precipitation assistant. In the present study,

the wastewater of the Emet boric acid production plant contains magnesium cations forming the magnesium hydroxide and the formed magnesium hydroxide exhibited supporting effect of arsenic removal as in the study of Sugita and coworkers (Sugita et al. 2023). The mentioned authors reported combined effects of MgO, Mg(OH)₂, MgCO₃, CaO, Ca(OH)₂ and CaCO₃ on arsenate removal (Sugita et al. 2023).

Mechanism of removal and the feasibility of the study

The concentrations of Emet boric acid production plant wastewater contaminants are 3956 mg/L SO₄⁻², 2541 mg/L boron and 36.4 mg/L total arsenic (III + V). The boron types found in Emet boric acid wastewater are monoborate and boric acid at natural wastewater pH of 5.32–5.69 (Figs. 3 and 4). The XRD patterns of raw calcium hydroxide and product of the adsorption are given in Fig. 13A and B. As seen in Fig. 13A and B, there are no new crystal structures at removal conditions for 20 $^{\circ}\text{C}$ and the adsorption was determined as physical for boron, sulphate and arsenic. Similarly, it was reported that boron precipitation by calcium hydroxide at room temperature did not produce any calcium borate compound and binding was physical (Tsai and Lo 2011). As the feasibility of the process, the reaction product containing calcium hydroxide, boron, sulphate and arsenic can be considered as raw material for boric acid production, and this product can be reused by adding gradually to boric acid production in the real process. However, this usage of the calcium hydroxide sludge may cause the increase of pollution in load. Therefore, the addition of the calcium hydroxide sludge to the production process should be continuous and little. After addition of sludge, the sulphate

Fig. 10 pH–Adsorbent amount interaction for boron, sulphate and arsenic removal



and arsenic increase in the reactor can be eliminated by filtration of gypsum, a calcium sulphate, adsorbing arsenic. Boron can be left in the reactor for crystallising again. We thought that as the addition of sludge after treatment to the leaching reactor should be at low amounts, there would not be any problem. This subject also is a different

investigation subject in this area. We thought that investigation of addition conditions of the sludge again to the leaching reactor would solve other important problems for the Emet boric acid production plant wastewaters. The addition of calcium hydroxide sludge to the boric acid production process has been already applied in Bandırma

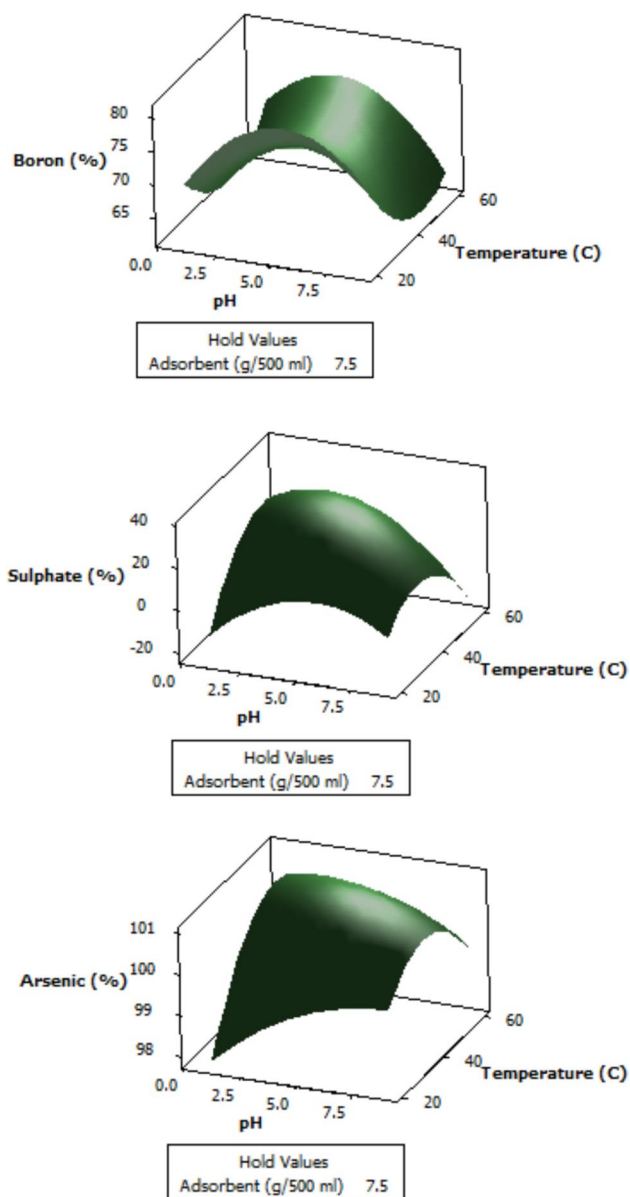


Fig. 11 pH–Temperature interaction for boron, sulphate and arsenic removal

Boric Acid Production Factory in Türkiye. However, its addition conditions should be investigated. The residual sulphate and boron from calcium hydroxide treatment of the wastewater was removed by Selion SBA 2000 strong basic resin for sulphate and Purolite S 108 specific boron resin for boron (Fig. 14A, B). Meanwhile, practically almost 99.9% removal percentages for boron and sulphate were obtained after calcium hydroxide treatment and given in Fig. 14A–B. The calcium hydroxide–treated wastewater pH in the present study is around 12, and after ion-exchange treatment, the pH of the solutions is above 8 for

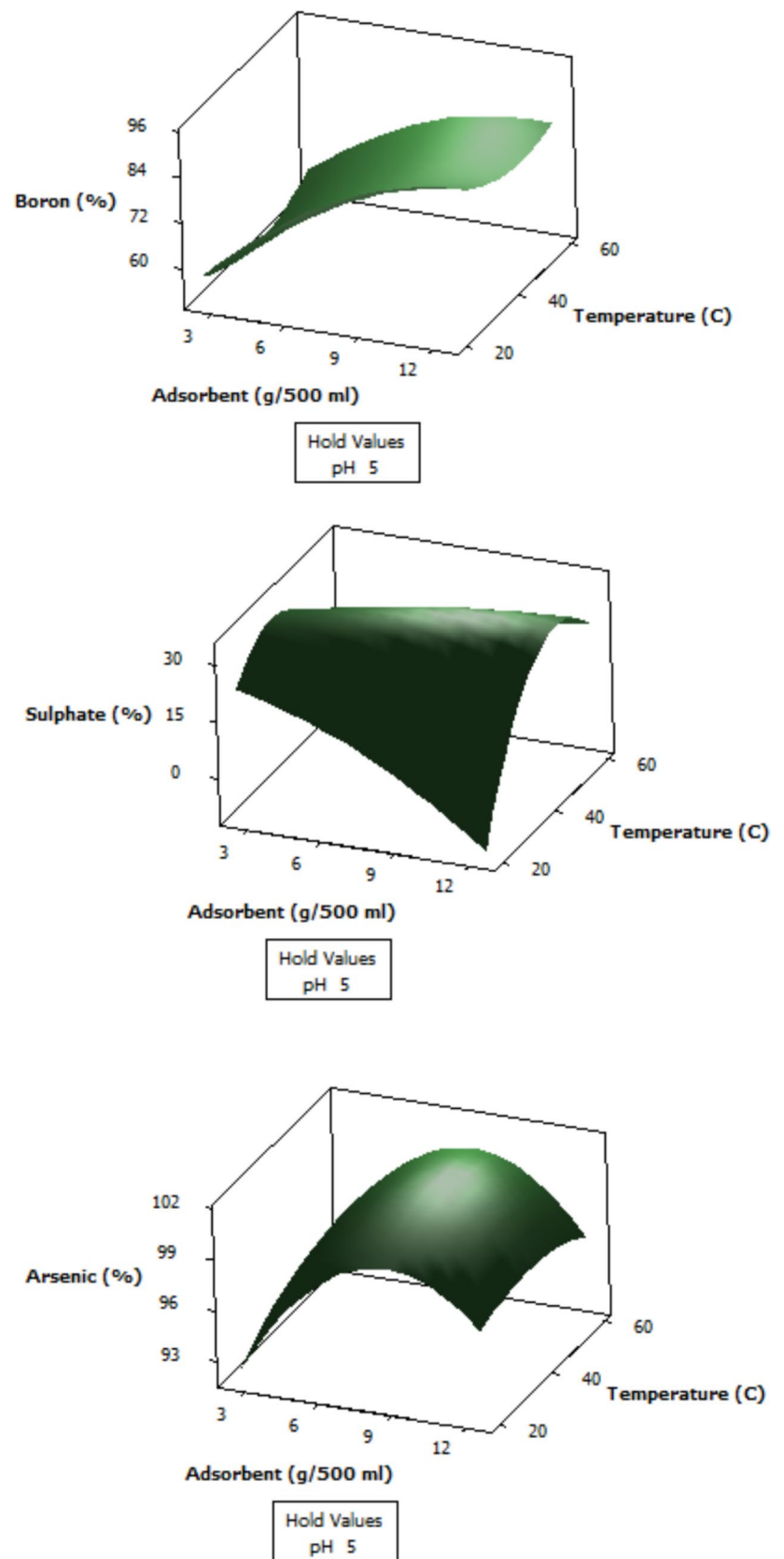
sulphate residue treatment and below 8 for boron residue treatment. These pH ranges are constant and the initial pH should be arranged before ion exchange of residue sulphate and boron removals. pH adjustment may only be necessary in the case of treated wastewaters used in the boric acid production. Similar second step removal processes such as ion exchange or reverse osmosis were proposed after boron removal by calcium hydroxide in the study of Tsai and Lo (2015). XRD picks of raw calcium hydroxide and adsorption product showed that there is not any crystal structure formation and therefore the adsorption of boron, sulphate and arsenic occurred by physical binding. The pick shortening from raw calcium hydroxide to reaction product calcium hydroxide was probably due to pollutant adsorption, calcination and framework jamming. The studied mini-reactor can be upgraded by ratio proportion approach to a real reactor. The treated wastewater by the calcium hydroxide and ion exchange process can include only a small degree of calcium and it would be free from other ions. Therefore, there would be no problem for water reuse in the process. Magnesium can precipitate at pH above 9. As can be seen from the optimisation studies, boron, sulphate and arsenic (III) removal percentages were calculated at optimum conditions as 87.94, 23.95 and 98.36%, respectively. The pollution problems in the Emet boric acid production plant can be given as follows:

1. The plant produces mainly boron-, sulphate- and arsenic-containing wastewater, and this wastewater could be treated by calcium hydroxide and ion-exchange processes. However, this wastewater can be treatable with membrane filtration, electrocoagulation and solvent extraction in future studies. The treated wastewater can be reused in the process.
2. The produced gypsum containing arsenic, boron and impurity clays needs extra treatment for safe storage. Therefore, arsenic and boron decrepitation from this clayish solid waste should be investigated.
3. In the mine field, sometimes floor waters containing boron are produced, and they should be treated and boron should be recovered. For this purpose, an ion-exchange process can be applied.
4. The excavated soils in the mine field can include boron, and they should be evaluated.

Conclusion

In this study, boron, sulphate and total arsenic (III) removal from boric acid production plant wastewater was studied and optimised for calcium hydroxide using

Fig. 12 Adsorbent amount–Temperature interaction for boron, sulphate and arsenic removal



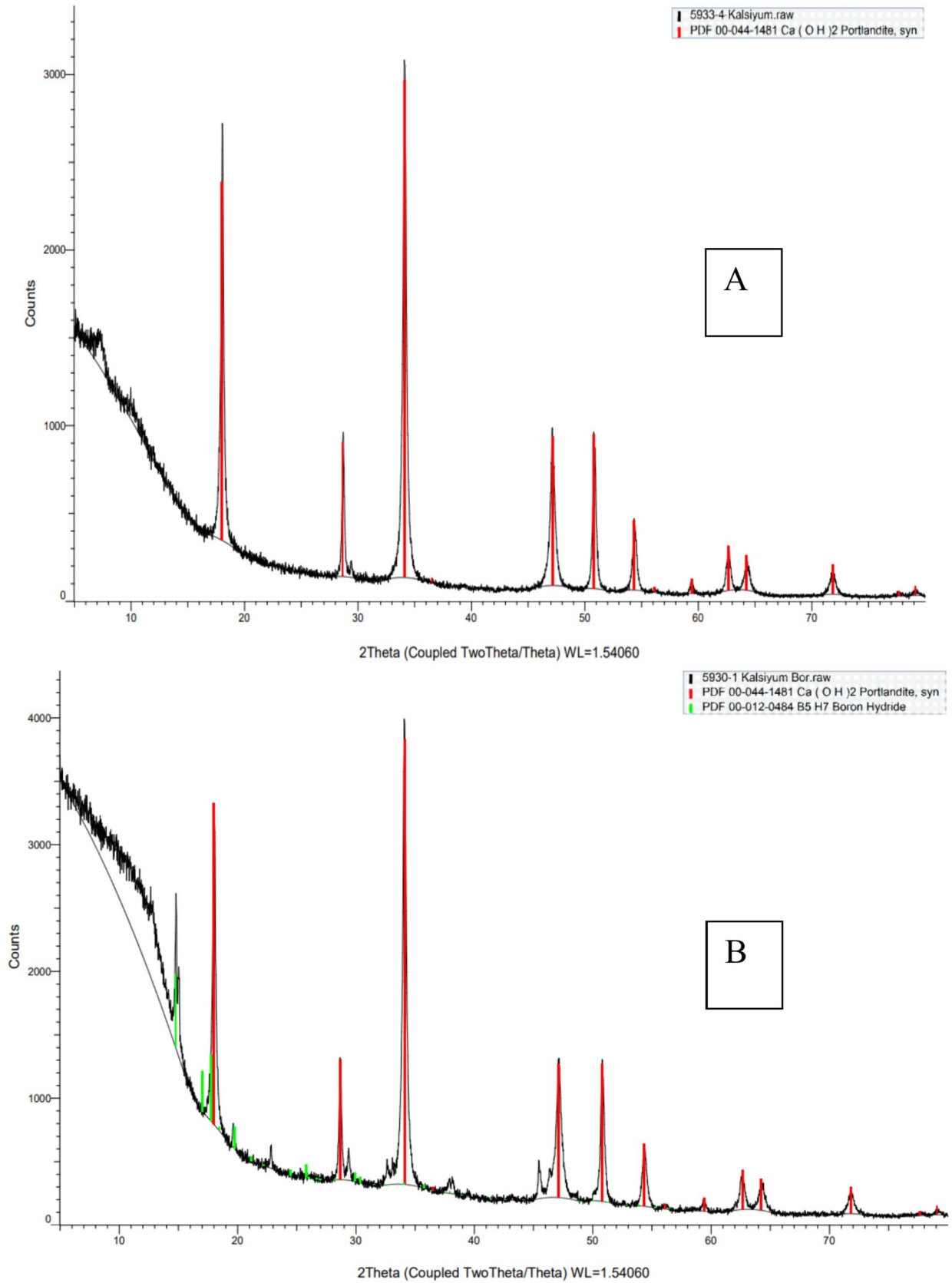


Fig. 13 XRD pattern of calcium hydroxide (A) before and (B) after adsorption (natural pH (5.88), 20 g/500 mL, 200 rpm, 21.7 °C, 500 mL, 150 min)

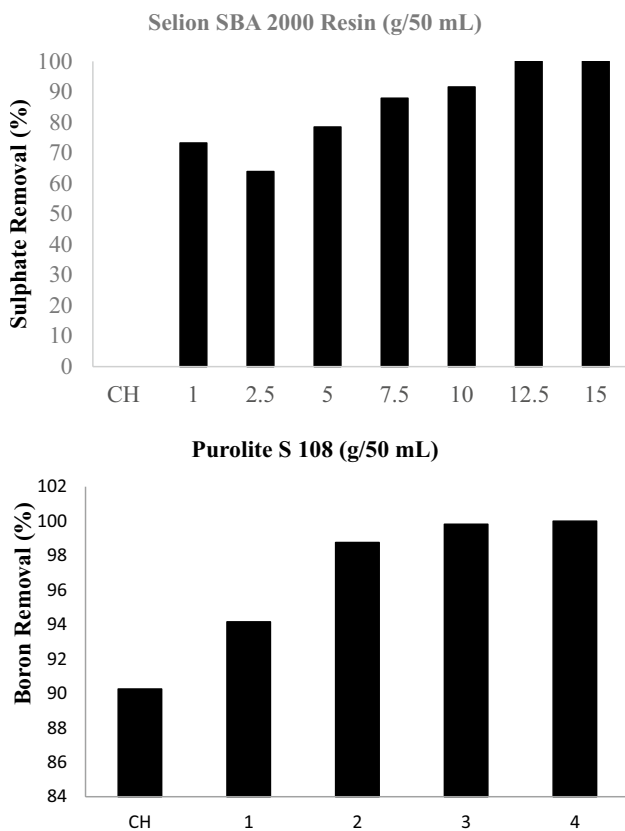


Fig. 14 Boron and sulphate removal after calcium hydroxide treatment of wastewater. CH: pH 5.58, 15 °C, 200 rpm, 7.5 g, 150 min. Sulphate-Resin: pH 8, 20 °C, 200 rpm, 50 mL, 24 h. Boron-Resin: pH 8, 20 °C, 200 rpm, 3.5 h, 50 mL

Minitab 16.0 program. The conclusions of this study can be summarised as follows:

- Optimum initial pH for boron removal was obtained as 5.32 due to the stripping effect of hydroxy ion at high pH.
- Optimum temperature for boron removal was obtained as 20 °C due to the exothermic nature of the removal.
- Optimum calcium hydroxide dosage for boron removal was obtained as 7.5 g/500 mL due to decreasing concentration gradient at high dosages.
- Optimum stirring speed was determined as 300 rpm.

The process was determined as exothermic (negative enthalpy) and adsorption of boron on calcium hydroxide has an increasing adsorption–desorption rate due to positive entropy. Also, low enthalpy showed the physical adsorption of boron. While sulphate adsorption was exothermic, arsenic adsorption was unclear. Activation energy had a positive value as a result of the energy

taking from reaction medium. Boron reaction controlling mechanisms were determined as particle diffusion and chemical reaction based on two different analysis approaches. Kinetics of boron removal obeyed the second-order kinetic model rather than zero-order and first-order models. Boron, sulphate and arsenic adsorption was optimised by applying central composite design to evaluate interactions and the main effect of parameter in removal by calcium hydroxide. All the parameters were unimportant for boron and sulphate, but model constant, solid and solid–solid interaction were important for arsenic. As can be seen in Fig. 10, boron removal increased at moderate pH and high adsorbent amount interaction. Sulphate removal increased at moderate pH and moderate adsorbent amount interaction. Arsenic removal increased at moderate adsorbent amount and high pH interaction. It is clear from Fig. 11 that boron removal increased at moderate pH and minimum and maximum temperature interactions. Sulphate removal increased at moderate pH and moderate temperature interaction. Arsenic removal increased at moderate pH and moderate temperature interaction. In Fig. 12, boron removal increased at high adsorbent amount and constant temperature interaction. Sulphate removal increased at high adsorbent amount and moderate temperature interaction. Arsenic removal increased at moderate adsorbent amount and moderate temperature interaction. The products of reaction of Emet boric acid production plant wastewater after calcium hydroxide adsorption are in non-crystallised form. As a feasibility and advantage of the method, this end-product can be used in boric acid production in a real system by gradually adding the reaction product to the colemanite–sulphuric acid system. Thus, there will not be any sludge to discharge to the environment. The applied removal by calcium hydroxide and advanced removal by the ion-exchange resins were concluded as effective for the treatment of Emet boric acid production plant wastewater so that the treated wastewater could be reused in the production.

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Author contribution All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Mustafa Korkmaz. The first draft of the manuscript was written by Mustafa Korkmaz, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript. This manuscript is from the Doctorate thesis of Dr. Mustafa Korkmaz, and Prof. Dr. Ahmet Günay was the supervisor of the thesis.

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Data availability The given data in this study were reported in the Doctorate thesis of Dr. Mustafa Korkmaz in Türkiye, and the thesis number is 802,744.

Declarations

Ethical approval There is no ethical approval required and this study is related to water pollution control.

Consent to participate This study does not require any consent to participate.

Consent to publish The authors give the consent to publish.

Conflict of interest The authors declare no competing interests.

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