

## Boron removal by means of chemical precipitation with calcium hydroxide and calcium borate formation

Alper Erdem Yilmaz<sup>\*,†</sup>, Recep Boncukcuoğlu\*, Serkan Bayar\*, Baybars Ali Fil\*, and Mehmet Muhtar Kocakerim\*\*

<sup>\*</sup>Department of Environmental Engineering, Atatürk University, Erzurum, Turkey

<sup>\*\*</sup>Department of Chemistry, Science Faculty, Çankırı Karatekin University, Çankırı, Turkey

(Received 21 November 2011 • accepted 20 March 2012)

**Abstract**—Boron removal was investigated by chemical precipitation from aqueous solutions containing boron using calcium hydroxide. pH, initial boron concentration, amount of  $\text{Ca}(\text{OH})_2$ , stirring speed and solution temperature were selected as operational parameters in a batch system. The highest boron removal efficiency was reached at pH 1.0. Increasing initial boron concentration and amount of calcium hydroxide raised to boron removal efficiency. Boron removal efficiency was highest at a stirring speed of 150 rpm. The most important parameter affecting boron removal efficiency was solution temperature. Increasing solution temperature increased importantly boron removal. XRD analysis showed that  $\text{CaB}_2\text{O}_3(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ , which is a borate mineral called inyoite, occurred between  $\text{Ca}(\text{OH})_2$  and borate ions. As a result of the obtained experimental data, when the optimum operational conditions were selected, over 96% of boron removal efficiency was reached by this method.

Key words: Boron, Removal, Recovery, Precipitation, Inyoite

### INTRODUCTION

Boron has a number of minerals, mostly calcium and/or sodium borates, such as colemanite ( $2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ), ulexite ( $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 5\text{B}_2\text{O}_3 \cdot 16\text{H}_2\text{O}$ ) and tincal ( $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$ ), etc. In nature, boron appears in the following forms: (1) mineral (borosilicates and borates), (2) adsorbed by clays, (3) adsorbed by organic matter, and (4) in aqueous solution. Boron has a variety of applications including various boron fertilizers, insecticides, corrosion inhibitors in anti-freeze formulations for motor vehicles and other cooling systems, buffers in pharmaceutical and dyestuff production, and the use of boron compounds for moderator in nuclear reactor, where anthropogenic water-soluble boron compounds are discharged to aqueous environment [1].

It is estimated that Turkey has about 72% of the boron reserves of the world. The known borate reserves in Turkey are located in four main districts, namely Emet, Bigadiç, Kırka and Mustafa Kemal Pasa [2]. Boron accumulates very fast in soils irrigated with boron-containing wastewaters because of difficulty of washing it. Boron compounds passing to soil with surface waters and groundwater form many complexes with heavy metals, such as Pb, Cd, Cu, and Ni, and these complexes are more toxic than heavy metals forming them [3]. The main sources of boron from wastes, whose presence is detected in surface waters, are urban wastes rich in detergents and cleaning products; and industrial wastes, which can come from a wide range of different activities as well as several chemical products used in agriculture [4].

It is present in living tissue in low concentrations (about  $1 \text{ mgL}^{-1}$ ) and is probably an essential micronutrient for the living [5]. The WHO has given a preliminary limit of  $0.3 \text{ mgL}^{-1}$  for drinking water. The EU regulations are suggesting a limit of  $1.0 \text{ mgL}^{-1}$ . Most of

surface and underground waters are below this limit; however, boron contamination of waters is a world-wide concern. Some industrial wastewaters and thermal waters contain high concentration of boron. The tendency of boron to accumulate in vegetable tissues constitutes a potential hazard to the health of those consuming food and water with high boron content. As a result, although boron is vital as a micronutrient element for plants' growth, it can cause hazardous effects at higher concentrations. For this reason, boron levels in drinking and irrigation waters must be kept under control. Boron removal from water is an important subject worldwide, which has recently attracted great attention. Because inorganic boron compounds are antiseptics, conventional biological treatment methods cannot be used for boron removal from wastewaters. A variety of treatment processes have been developed for boron elimination from water, including adsorption [6-9], ion exchange [10-13], reverse osmosis [14], electrocoagulation [15], electrodialysis [16], sorption-membrane filtration [17] and precipitation, which is a simple, easily automated and widely applied process [18,19].

In this study, chemical precipitation process has been carried out for boron removal. For this purpose, calcium hydroxide, a less commonly used in the industrial wastewater treatment was used. The flocks were then separated from the aqueous solution by means of physical sedimentation. The process was examined under different values of pH, initial boron concentrations, temperature, amount of  $\text{Ca}(\text{OH})_2$ , and stirring speed, in order to determine optimum operating conditions. The results of this study provided to the recovery of boron which is economically very valuable. The results contributed to the protection of natural resources.

### MATERIALS AND METHODS

#### 1. Reagents

Wastewater samples used in the experiments were prepared synthetically using  $\text{H}_3\text{BO}_3$  having 99.99% of purity from upper grade

<sup>†</sup>To whom correspondence should be addressed.  
E-mail: aerdemy@atauni.edu.tr

**Table 1. The parameters used in the experiments and their values**

Parameters	Parameter values
pH	0.5, 1.0, 2.0, 4.0, 6.0
Initial boron concentration ( $\text{mg}\cdot\text{L}^{-1}$ )	250, 500, 1000, 2500
Temperature (K)	293, 313, 333, 353
Ratio of solid/liquid ( $\text{g}\cdot\text{mL}^{-1}$ )	2.5/500, 5.0/500, 10.0/500
Stirring speed (rpm)	75, 150, 300

quality. The solutions with boron concentration of 250, 500, 1,000 and 2,500  $\text{mg}\cdot\text{L}^{-1}$  were prepared by dissolving enough amounts of  $\text{H}_3\text{BO}_3$  dried at  $105^\circ\text{C}$  in distilled water. Calcium hydroxide used for the experiments has 99.99% of purity from upper grade quality. The parameters used in the experiments were solution pH, initial boron concentration, temperature, amount of  $\text{Ca}(\text{OH})_2$ , and stirring speed. These parameters and their values are given in Table 1.

## 2. Experimental Setup

In the batch system used for removing boron from synthetic wastewater by precipitation, the temperature of the reactor was controlled with a SELECTA P100 thermostat. The pH of the solution was adjusted with a WTW P4 multi-meter. In each experiment, after 500 mL wastewater was put into the reactor and pH was adjusted, a weighted amount of the calcium hydroxide was added in the reactor. The desired temperature was maintained within  $\pm 0.5^\circ\text{C}$  and reactor content was stirred with stirrer motor with tachometer at a desired stirring speed. The precipitates in the samples taken in desired periods were separated by being filtrated by  $0.2\ \mu\text{m}$  cellulose acetate membrane filter. The amount of boron reacted with the calcium hydroxide was calculated from boron concentration in solution. The analytical determination of boron was done spectrophotometrically by Carmine method [20]. For this purpose, a Shimadzu 160 Model spectrophotometer was used at 585 nm of wavelength. Experiments were reduplicated.

## 3. Powder X-ray Diffraction Analysis (XRD)

XRD analysis was carried out with a Rigaku D/MAX diffractometer ( $\text{Cu K}_\alpha$ ). The X-ray generator worked at a power of 40 kV and 40 mA, the goniometer was equipped with a graphite monochromator in the diffracted beam. The patterns were collected in the angular range from  $10^\circ$  to  $80^\circ$  with  $0.05^\circ$  of step size. The powder patterns were analyzed according to the Rietveld method [21], using the software MAUD running on a personal computer. Crystalline phases were identified using the database of the International Centre for Diffraction Data for Inorganic Substances (Inorganic Crystal Structure Database).

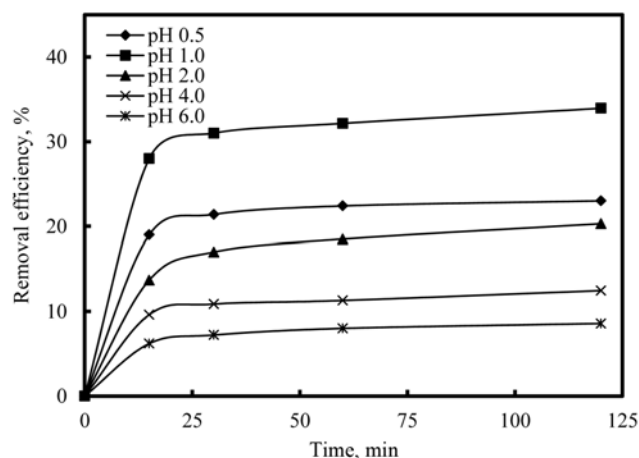
# RESULTS AND DISCUSSION

## 1. The Effects of Parameters

In this study, we investigated the effects of parameters such as initial pH, ratio of solid/liquid, boron concentration, temperature and stirring speed at the reaction times up to 120 minutes.

## 2. The Effect of pH

It has been established that the pH has a considerable influence on the performance of chemical precipitation process. The effect of initial pH on the boron removal was examined at 0.5, 1.0, 2.0, 4.0 and 6.0 pH's using 500 ml wastewater containing boron of 1,000



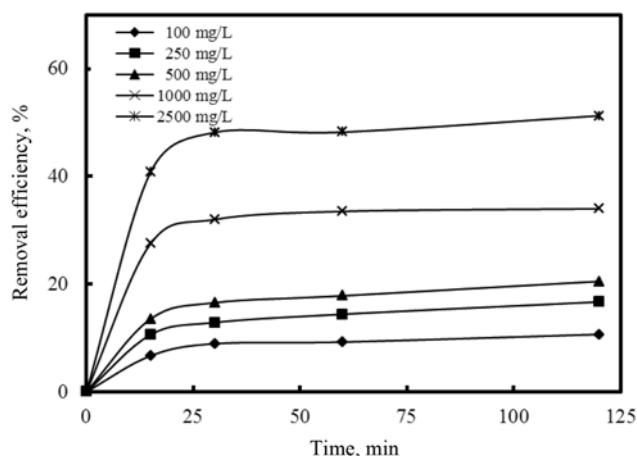
**Fig. 1. The effect of initial pH on the boron removal (solution temperature: 293 K, initial boron concentration: 1,000  $\text{mg}\cdot\text{L}^{-1}$  and stirring speed: 150 rpm).**

$\text{mg}\cdot\text{L}^{-1}$ . The amount of  $\text{Ca}(\text{OH})_2$  of 10 g, solution temperature of 293 K and stirring speed of 150 rpm were kept constant in the experiments. The initial pH of solution was adjusted by adding concentrated  $\text{H}_2\text{SO}_4$ . Calcium hydroxide was added to solution after pH was adjusted. Boron removal increased with increasing the pH up to 1.0, and then decreased with increasing pH. Solution pH with added  $\text{Ca}(\text{OH})_2$  was exchanged as follows. Depending on the different starting pH values, the final pH of the solution was 10.5, 11.7, 12.2, 12.7 and 13.0 for 0.5, 1.0, 2.0, 4.0 and 6.0 pH, respectively. Naturally, solution pH increased with added  $\text{Ca}(\text{OH})_2$ , but this increase differentiated as function of initial pH.

Boric acid dissolves in water to form various borate ions which their compositions change as a function of solution pH and begins to dissociate into monoborate ions at  $\text{pH} > 12$ . The formation of monoborate decreased to react between  $\text{Ca}(\text{OH})_2$  and boron ions. Therefore, increasing pH caused to decrease boron removal efficiency. While boron removal efficiency reached to 35% at pH 1.0, the value of the removal decreased to 8% at pH 6. The results obtained are shown graphically in Fig. 1 for 1,000  $\text{mg}\cdot\text{L}^{-1}$  boron concentration.

## 3. The Effect of Initial Boron Concentration

In this study, boron concentration was chosen high because boron concentration from boron industry wastewater was quite high. The effect of initial boron concentration on the boron removal was examined with solutions including boron of 100, 250, 500, 1,000 and 2,500  $\text{mg}\cdot\text{L}^{-1}$ . The amount of  $\text{Ca}(\text{OH})_2$  of 10 g, optimum pH of 1.0, solution temperature of 293 K and stirring speed of 150 rpm were kept constant in the experiments. 10 g calcium hydroxide was added to boron-containing wastewater after its pH was adjusted. The samples collected at given time interval were filtered and analyzed by colorimetric method. The obtained experimental data showed that increasing initial boron concentration increased boron removal efficiency. When boric acid dissolves in water, it is ionized to borate ions and, in general, only monoborate ions exist at lower boron concentration; several polyborate ions exist at higher boron concentration [22]. It was considered that boron removal efficiency of wastewater containing higher boron concentration increased due to higher polyborate ions at higher boron concentration. While removal efficiency of the solution with 100  $\text{mg}\cdot\text{L}^{-1}$  initial boron concentration

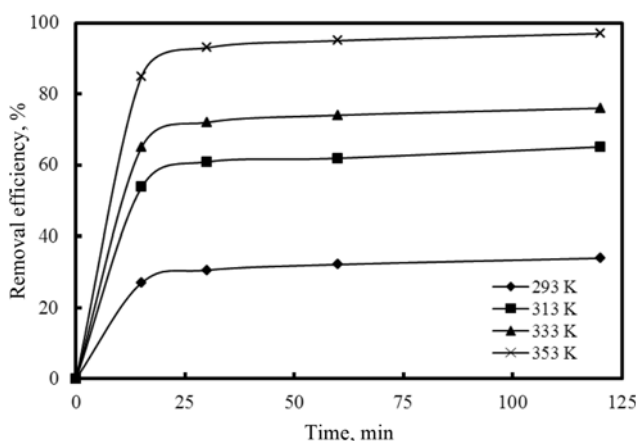


**Fig. 2.** The effect of initial boron concentration on the boron removal (solution temperature: 293 K, pH: 1.0 and stirring speed: 150 rpm).

approximately reached 11%, this efficiency of the solution with 2,500 mg/L initial boron concentration reached to 52%. The change in concentration led to a change of the final solution pH. Depending on the different initial boron concentration, the final pH of the solutions was 12.55, 12.37, 12.2, 11.7 and 11.2 for 100, 250, 500, 1,000 and 2,500 mg/L, respectively. The results obtained are shown graphically in Fig. 2.

#### 4. The Effect of Solution Temperature

The effect of temperature on the boron removal was examined with 293, 313, 333 and 353 K. Initial boron concentration of 1,000 mgL<sup>-1</sup>, stirring speed of 150 rpm, amount of Ca(OH)<sub>2</sub> of 10 g and optimum pH of 1.0 were kept constant in the experiments. It was seen that increasing solution temperature increased boron removal efficiency. Temperature had an important effect on boron removal, and boron removal efficiency was more effective at higher temperatures. The results obtained are shown graphically for 1,000 mgL<sup>-1</sup> boron concentration in Fig. 3. The temperature has two major effects on the removal process. Increasing the temperature is known to increase the rate of diffusion of the borate ions across the external boundary layer and in the internal pores of the Ca(OH)<sub>2</sub> particle,



**Fig. 3.** The effect of solution temperature on the boron removal (initial boron concentration: 1,000 mg·L<sup>-1</sup>, pH: 1.0, stirring speed: 150 rpm and ratio of solid/liquid: 10 g).

owing to the decrease in the viscosity of the solution. In addition, temperature change will change the equilibrium capacity of the Ca(OH)<sub>2</sub> for particular borate ions.

This method has succeeded in the recovery of boron from solution. The studies in literature generally focused on the removal of boron from solution [23-27]. The results of this study showed that boron was removed from aqueous solution and the product, which can be of economic value, was obtained. A similar method was used by Remy et al. In the study reported by Remy et al., it was stated that under optimal conditions such as 50 g L<sup>-1</sup> of powdered calcium hydroxide, a temperature of 90 °C, and process time of 2 h, the residual boron concentration in solution was reduced from 700 to less than 50 mg L<sup>-1</sup>. In this study, the X-ray diffractometric spectrum of the precipitate does not allow the indexing of borates [28]. In another study that used the method of hydrothermal treatment, fluorine, and boron-containing waste waters were investigated. The reported results showed that the hydrothermal mineralization treatment with the Ca(OH)<sub>2</sub> mineralizer is an effective technique to recover boron and fluorine from wastewater. In this study, fluorine and boron were recovered as CaF<sub>2</sub> and Ca<sub>2</sub>B<sub>2</sub>O<sub>5</sub> [29]. In the study by Tsai et al., it was compared with microwave heating and conventional heating methods. The results obtained showed that a more effective method of microwave heating. The experimental results showed that boron recovery efficiency reached 90% within 10 min, and crystals of Ca<sub>2</sub>B<sub>2</sub>O<sub>5</sub>·H<sub>2</sub>O were found in the precipitates as indicated by the XRD analysis. For the case of P-addition and the microwave method, boron recovery efficiency reached 99% within 10 min, and CaHPO<sub>4</sub>·H<sub>2</sub>O, CaHPO<sub>4</sub> and Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> were formed [30]. The wastewater containing boron has been subjected to hydrothermal treatment and it was observed that boron removal was effective. The precipitates were characterized by SEM, XRD, and XPS, and confirmed that it was calcium borate (Ca<sub>2</sub>B<sub>2</sub>O<sub>5</sub>·H<sub>2</sub>O) [31]. The results obtained in this study are also consistent with the literature. Different boron such as CaB<sub>3</sub>O<sub>6</sub>(OH)<sub>5</sub>·4H<sub>2</sub>O (Inyoite) was obtained in this study.

The change in initial solution temperature has led to a change of the final solution pH because increasing solution temperature was changed to reaction rate between borate ions and Ca(OH)<sub>2</sub>. Depending on the different initial solution temperature, the final pH of the solutions was 11.73, 11.50, 11.22, and 10.92 for 293, 313, 333 and 353 K, respectively.

#### 5. The Effect of Amount of Ca(OH)<sub>2</sub>

The effect of dosage of Ca(OH)<sub>2</sub> on the boron removal was examined by adding 2.5, 5 and 10 g of calcium hydroxide to the wastewater after solution pH was adjusted. Initial boron concentration of 1,000 mgL<sup>-1</sup>, stirring speed of 150 rpm, solution temperature of 353 K and optimum pH of 1.0 were kept constant in the experiments. Increasing amount of calcium hydroxide increased boron removal efficiency. This situation is owing to increasing amount of calcium hydroxide per borate ions in solution. With addition of the amount of Ca(OH)<sub>2</sub>, the final pH value of the solution increased. Depending on the different the amount of Ca(OH)<sub>2</sub>, the final pH of the solution was 10.30, 11.60, and 10.92 for 2.5, 5.0 and 10.0 g, respectively. The obtained results are shown graphically for 1,000 mgL<sup>-1</sup> boron concentration in Fig. 4.

#### 6. The Effect of Stirring Speed

The effect of stirring speed on the boron removal was examined

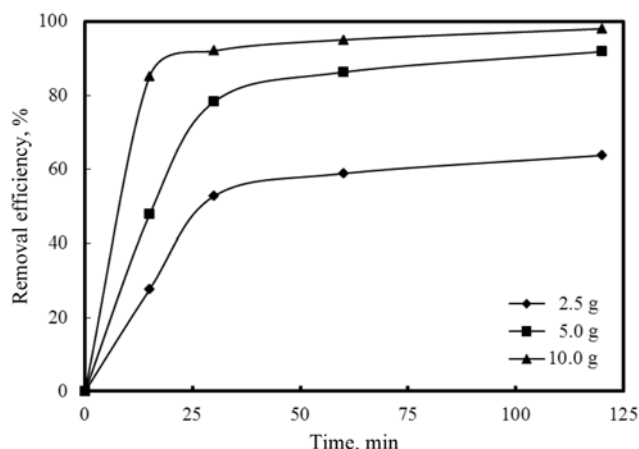


Fig. 4. The effect of ratio of solid/liquid on the boron removal (initial boron concentration:  $1,000 \text{ mg}\cdot\text{L}^{-1}$ , solution temperature:  $353 \text{ K}$ , pH: 1.0 and stirring speed:  $150 \text{ rpm}$ ).

with 75, 150 and  $300 \text{ rpm}$ . Initial boron concentration of  $1,000 \text{ mg}\cdot\text{L}^{-1}$ , amount of  $\text{Ca}(\text{OH})_2$  of  $10 \text{ g}$ , optimum pH of 1.0 and solution temperature of  $353 \text{ K}$  were kept constant in the experiments.  $10 \text{ g}$  calcium hydroxide was added to each boron-containing wastewater after their pHs were adjusted. The samples were collected at a given time interval, filtered and analyzed. As a result of obtained experimental data, the highest boron removal efficiency was obtained at a stirring speed of  $150 \text{ rpm}$ . At a stirring speed of 75 and  $300 \text{ rpm}$ , boron removal efficiencies were lesser. When  $75 \text{ rpm}$  of stirring speed was investigated,  $\text{Ca}(\text{OH})_2$  added to reactor was not homogeneously mixed in the reactor and it was observed that  $\text{Ca}(\text{OH})_2$  precipitated. This situation caused to decrease the reaction rate between  $\text{Ca}(\text{OH})_2$  and borate ions in the solution. When the effect of  $300 \text{ rpm}$  of stirring speed on boron removal was investigated, it was observed that this stirring speed prevented influence of  $\text{Ca}(\text{OH})_2$  on pollutant. It was thought that increasing stirring speed caused the increase of centrifugal force between  $\text{Ca}(\text{OH})_2$  and pollutant. Therefore, this situation decreased boron removal. The variation of stirring speed also affected the final pH value of solution. The final

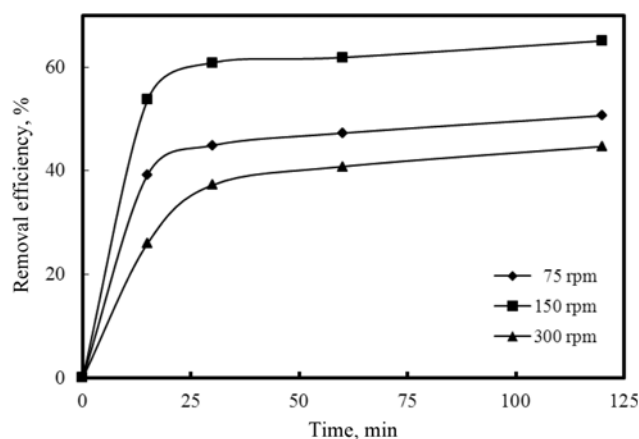


Fig. 5. The effect of stirring speed on the boron removal (initial boron concentration:  $1,000 \text{ mg}\cdot\text{L}^{-1}$ , solution temperature:  $313 \text{ K}$ , pH: 1.0 and ratio of solid/liquid:  $10 \text{ g}$ ).

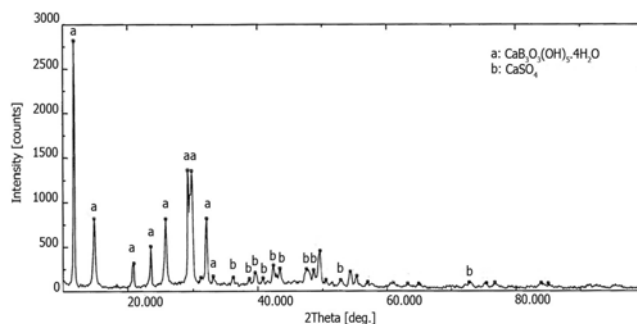
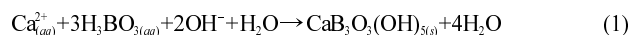


Fig. 6. X-ray diffraction diagram of obtained solid.

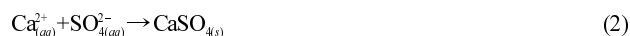
pH values of solution increased because increasing stirring speed caused the increase of  $\text{Ca}(\text{OH})_2$  dissolution. Depending on the different the stirring speed, the final pH of the solutions was 10.25, 10.90, and 11.55 for 75, 150 and  $300 \text{ rpm}$ , respectively. The results are shown graphically for  $1,000 \text{ mg}\cdot\text{L}^{-1}$  boron concentration in Fig. 5.

### 7. XRD Analysis

The solid phase formed as a result of adsorption/precipitation experiments was analyzed by XRD measurements using  $\text{CuK}\alpha$  radiation. Formed solid has a formation of crystallized construction. Fig. 6 shows the XRD pattern of the precipitate obtained from synthetic wastewater with  $1,000 \text{ mg}\cdot\text{L}^{-1}$  of boron where the diffraction peaks for both  $\text{CaB}_3\text{O}_3(\text{OH})_5\cdot 4\text{H}_2\text{O}$  (Inyoite, Card no: 371459) and  $\text{CaSO}_4$  were identified. This also suggests that  $\text{CaB}_3\text{O}_3(\text{OH})_5\cdot 4\text{H}_2\text{O}$  crystals would be formed on the surface of the undissolved  $\text{Ca}(\text{OH})_2$  crystalline surface.  $\text{CaB}_3\text{O}_3(\text{OH})_5\cdot 4\text{H}_2\text{O}$  is formed by reaction between borate anion and  $\text{Ca}(\text{OH})_2$  in the solution. To prevent redissolution of  $\text{CaB}_3\text{O}_3(\text{OH})_5\cdot 4\text{H}_2\text{O}$ , solution containing precipitate was rapidly cooled at the end of reaction time. According to this,  $\text{Ca}^{2+}$  and borate ions react as follows:



On the other hand,  $\text{CaSO}_4$  seen in XRD is due to  $\text{H}_2\text{SO}_4$  used for adjusting pH. In this manner,  $\text{Ca}^{2+}$  from  $\text{Ca}(\text{OH})_2$  and  $\text{SO}_4^{2-}$  from  $\text{H}_2\text{SO}_4$  react as follows:



### 8. Empirical Model

An empirical model was developed to relate the critical parameters such as pH, initial boron concentration, solution temperature, dosage of  $\text{Ca}(\text{OH})_2$ , stirring speed and reaction time for boron removal using chemical precipitation process. Based on the operational parameters, an empirical equation may be given to calculate the optimal boron removal rate, and also, the formation rate of inyoite crystallized by precipitating with  $\text{Ca}(\text{OH})_2$ . In this study a manual approach was used for model calibration. Default values of parameters related to chemical precipitation processes were initially employed. Then, differences between predicted and observed values were noted and adjustments made in parameter values until an efficient match between observed and calculated values of desired variables was reached. Change in the default values of six model parameters gave a reasonable match for the investigated variables. Experimentally obtained values including pH, initial boron concentration, solution temperature, ratio of solid/liquid, stirring speed and reaction time were easily transferred on the Statistica 6.0 program as a

first step using user-friendly graphical icons. Some operational parameters of the chemical precipitation were entered to the Statistica 6.0 software. It is concluded that chemical precipitation is a viable process for boron removal of industrial effluent that contains excess boron. The results obtained by using various reaction parameters were used to investigate the chemical precipitation kinetics of the removal of the boron, and various reaction models were tested statistically for this purpose. Avrami has suggested a mathematical model crystallization system as follows.

$$-\ln(1-X)=k \cdot t^n \quad (3)$$

By statistical analyses it was determined that the best equation representing precipitation process here is Avrami model. Also, the values of  $-\ln(-\ln(1-X))$  vs.  $\ln t$  were plotted for each parameter and straight lines were obtained for each parameter. The plot of  $-\ln(-\ln(1-X))$  vs.  $\ln t$  is given in Fig. 7 for various temperatures. As seen from the figure, there is a linear relationship between  $-\ln(-\ln(1-X))$  and  $\ln t$ . To obtain an equation including all parameters used in the experiments, the relationship between  $k$  and the reaction parameters was examined. Assuming that the relation between  $k$ , and the temperature has the form of an Arrhenius equation, the values of  $k$ , vs.  $1/T$  were plotted; and from the slope of the straight line obtained, activation energy and the Arrhenius constant were calculated as 25,767

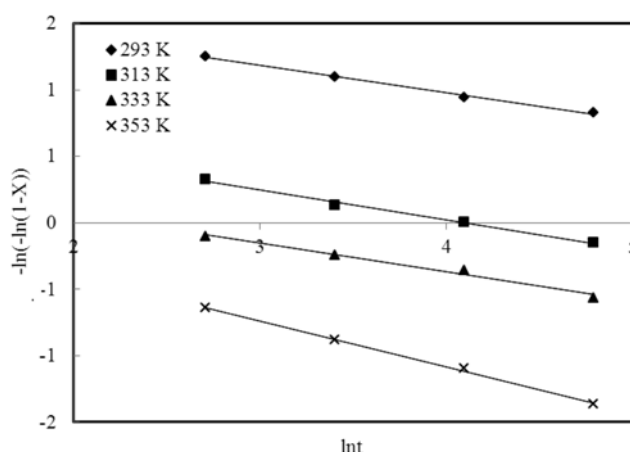


Fig. 7. Plot of  $-\ln(-\ln(1-X))$  versus  $\ln t$  for various temperatures.

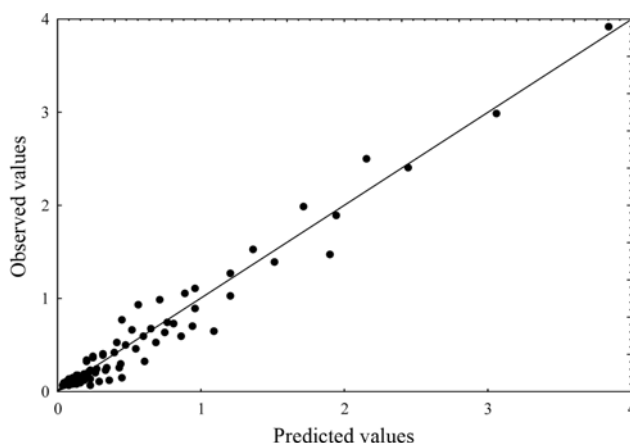


Fig. 8. Plot of predicted  $X$  versus observed  $X$ .

$J \cdot \text{mole}^{-1}$  and  $6,587 \text{ s}^{-1}$ , respectively. Finally, the rate equation for the removal of boron by chemical precipitation method can be expressed by the following model:

$$-\ln(1-X)=6587[H] \cdot [C]^{1.22} \cdot [S/L]^{0.81} \cdot [SS]^{-0.11} \cdot t^{0.35} \cdot e^{-(25767/RT)} \quad (4)$$

where,  $H$  is solution pH,  $C$  is boron concentration ( $\text{mg} \cdot \text{L}^{-1}$ ),  $S/L$  is solid/liquid ratio,  $SS$  is stirring rate (rpm),  $t$  is reaction time (min),  $R$  is gas constant,  $T$  is solution temperature (K). The plot of predicted  $X$  vs. observed  $X$  given in Fig. 8 shows that the kinetics model obtained very well fits the experimental results. The results show good agreement between the experimental data and the predictive equation.

## CONCLUSIONS

The following conclusions can be drawn from this study in which calcium hydroxide was used as precipitant for boron precipitation from synthetic wastewater containing boron and its derivatives. It was shown that this removal process considerably decreased the concentration of borate ion in aqueous solutions with a relatively high initial concentration of this ion, which was fixed at  $1,000 \text{ mgL}^{-1}$  of B in this study.

1. The highest boron removal efficiency was obtained at pH 1.0. The reason for this statement was considered is that powdered calcium hydroxide had not enough precipitant characteristic at higher pH than 1.0 and powdered calcium hydroxide dissolved at lower pH than 1.0.

2. The highest boron removal efficiency was obtained at solution containing  $2,500 \text{ mgL}^{-1}$  of boron. The reason being high boron removal efficiency at high initial boron concentration was considered that borate species in solution having high boron concentration changed from monoborate to polyborate.

3. Solution temperature has a very important effect on boron removal efficiency. At the experiments carried out with solutions having same initial boron concentration, while boron removal efficiency was 39% at 293 K, boron removal efficiency reached to 97% at 353 K. The result of the dominant effect of temperature on boron removal was considered as that increasing temperature changed to structure of calcium hydroxide. It was considered that the exchange of calcium hydroxide structure pertained to pore size, and the exchange of pore size has positive effects on boron removal.

4. The highest boron removal efficiency was reached to calcium hydroxide of 10 g when effect of amount of  $\text{Ca}(\text{OH})_2$  on boron removal. Boron removal efficiency increased because increasing the amount of calcium hydroxide increased the amount of precipitant reacting with constant pollutant.

5. The highest boron removal efficiency was obtained at 150 rpm.  $\text{Ca}(\text{OH})_2$  demonstrated a precipitating tendency at lower stirring speed (e.g. 75 rpm). It was considered that higher stirring speed decomposed to precipitant-borate formation in solution.

6. This study achieved not only the removal of the dissolved boron species from wastewater, but also the recovery of calcium borate mineral by the addition of  $\text{Ca}(\text{OH})_2$ . The process used in this study will be efficient on the environmental condition. The recovered  $\text{CaB}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$  in this study is one of the calcium borate ores that has been found in nature (Inyoite). Therefore, this technique will be effective on the environmental aspect compared with the conventional

removal techniques of boron.

## REFERENCES

1. R. Boncukcuoğlu, M. M. Kocakerim, E. Kocadağistan and M. T. Yılmaz, *Resour. Conserv. Recycl.*, **37**, 147 (2003).
2. N. Öztürk and D. Kavak, *J. Hazard. Mater. B*, **127**, 81 (2005).
3. H. F. Seiler, *Handbook on toxicity of inorganic compounds*, Marcel Dekker Inc., New York (1998).
4. A. E. Yılmaz, R. Boncukcuoğlu and M. M. Kocakerim, *J. Hazard. Mater.*, **144**, 101 (2007).
5. W. T. Barranco, P. F. Hudak and C. D. Eckhert, *Cancer Causes Control*, **18**, 71 (2007).
6. X. Li, R. Liu, S. Wu, J. Liu, S. Cai and D. Chen, *J. Colloid Interface Sci.*, **361**(1), 232 (2011).
7. M. Yurdako, Y. Seki, S. Karahan and K. Yurdako, *J. Colloid Interface Sci.*, **286**, 440 (2005).
8. S. Karahan, M. Yurdako, Y. Seki and K. Yurdako, *J. Colloid Interface Sci.*, **293**, 36 (2006).
9. D. Kavak, *J. Hazard. Mater.*, **163**, 308 (2009).
10. R. Boncukcuoğlu, A. E. Yılmaz, M. M. Kocakerim and M. Copur, *Desalination*, **160**, 159 (2004).
11. A. E. Yılmaz, R. Boncukcuoğlu, M. T. Yılmaz and M. M. Kocakerim, *J. Hazard. Mater.*, **117**, 221 (2005).
12. C. Yan, W. Yi, P. Ma and X. Deng, *J. Hazard. Mater.*, **154**, 564 (2008).
13. N. Kabay, I. Y. Ipek, I. Soroko and M. Makowski, *Desalination*, **241**, 167 (2009).
14. H. Koseoglu, B. I. Harman, N. O. Yigit and E. Guler, *Desalination*, **258** (2010).
15. A. E. Yılmaz, R. Boncukcuoğlu, M. M. Kocakerim and B. Keskinler, *J. Hazard. Mater. B*, **125**, 160 (2005).
16. Z. Yazicigil and Z. Oztekin, *Desalination*, **190**, 71 (2006).
17. J. Wolska and M. Bryjak, *Desalination*, **283**, 193 (2011).
18. T. Itakura, R. Sasai and H. Itoh, *Water Res.*, **39**, 2543 (2005).
19. M. M. F. Garcia-Soto and E. M. Camacho, *Sep. Purif. Technol.*, **48**, 36 (2006).
20. Franson, 21<sup>st</sup> Ed., M.A.H., APHA, AWWA and WPCF Press (2005).
21. J. Ghosh, S. K. Chattopadhyay, A. K. Meikap and S. K. Chatterjee, *J. Alloy. Compd.*, **453**, 131 (2008).
22. J. W. Na and K. J. Lee, *Ann. Nucl. Energy*, **20**, 455 (1993).
23. D. Hou, J. Wang, X. Sun and Z. Luan, *J. Hazard. Mater.*, **177**, 613 (2010).
24. A. E. Yılmaz, R. Boncukcuoğlu, M. M. Kocakerim and E. Kocadağistan, *Desalination*, **230**, 288 (2008).
25. N. Öztürk, D. Kavak and T. E. Köse, *Desalination*, **223**, 1 (2008).
26. Y. Cengeloglu, G. Arslan, A. Tor and I. Kocak, *Sep. Purif. Technol.*, **64**, 141 (2008).
27. O. P. Ferreira, S. G. Moraes, N. Durán and L. Cornejo, *Chemosphere*, **62**, 80 (2006).
28. P. Remy, H. Muhr, E. Plasari and I. Ouerdiane, *Environ. Progress*, **24**, 1 (2005).
29. T. Itakura, R. Sasai and H. Itoh, *Bullet. Chem. Soc. Japan*, **79**, 1303 (2006).
30. H. C. Tsai and S. L. Lo, *J. Hazard. Mater.*, **186**, 1431 (2011).
31. C. Irawan, Y. L. Kuo and J. C. Liu, *Desalination*, **280**, 1-3, 280 (2011).