# The Effect of Initial pH and Retention Time on Boron Removal by Continuous Electrocoagulation Process

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## Abstract

In this study, factors influencing boron removal via the continuous electrocoagulation process were investigated at lab-scale. Different influent pH values (4, 5, 6, 7.45 and 9) and contact times (10, 25, 50 and 100 min) were examined as variable parameters. Plate-type aluminium electrodes with 5 mm distance between them were used. All the experiments were conducted in continuous mode and the current density was kept constant at 5 A throughout the whole experimental period. The initial boron concentration was selected to be 1000 mg $L^{-1}$. The first set of experiments concerning the influence of the influent pH showed that the highest boron removal (67%) was obtained at pH=6 since it was the optimal pH for boron precipitation through aluminium borate formation. Under the constant current density of the study and with the initial pH adjusted to 6, increasing the duration of the electrocoagulation process from 10 to 100 min resulted in raising the boron removal from 45 to 79% during the second set of experiments. The greater duration of the electrocagulation process enabled higher aluminium dissolution, thus allowing the existence of a higher number of coagulants within the reactor. Moreover, it enhanced boron precipitation because of the longer contact time between the boron ions and the coagulants. After optimizing significant parameters such as the influent pH and the electrocagulation duration, the continuous electrocoagulation process was found to constitute an effective alternative for boron removal.

**Keywords** Boron, continuous electrocoagulation process, influent pH, electrocoagulation duration, contact time

## 1. Introduction

Boron (B) is a trace element widely distributed in the earth's hydrosphere and lithosphere. In the lithosphere, boron can be found in soil or rocks with its average concentration being 10 mg $kg^{-1}$ in the earth’s crust, thus taking up only 0.001% of the earth’s elemental composition [1-2]. In the hydrosphere, its average concentration is about 4.5 mg $L^{-1}$ in seawater, whereas its concentration varies from 0.3 to 100 mg $L^{-1}$ in groundwater [1-3]. In nature, elemental boron hasn't been found yet; it is traced in compounds together with other elements.

In the recent years, a significant increase in the boron concentration in surface water has been observed. The concentration increases/fluctuations among different areas are related to both natural and anthropogenic

factors. Weathering of rocks and leaching of salt deposits can be counted as natural causes. Then, boron deposits appear on the shoreline. Due to its high volatility, boron can be found in the rainfall at coastal areas. Industrial activities can additionally trigger an increase of the boron amount in surface waters. Boric acid ($BH_3O_3$) and boron salts are widely used as a preservative in many industrial sectors. Boron is also detected in the "acid rain" [4-6]. Recently, boron compounds have been utilized in the production of high-energy fuels, coolants and catalysts [7]. Hence, the boron concentration in surface water at industrial and urban areas is constantly increasing. Therefore, boron removal from water is particularly significant not only for countries with natural deposits but also for those with high industrial activity.

Electrocoagulation consists of an in-situ generation of coagulants by an electrical dissolution of iron or aluminium electrodes. The metal ions generation takes place at the anode; hydrogen gas is released from the cathode. The hydrogen gas would also help the flocculated particles to float out of the water, and therefore, the process is often called electroflocculation [8]. Typically, aluminium, iron, carbon, mild steel, graphite and titanium plates are used as electrodes in the electrocoagulation process. Iron and aluminium in specific have been reported to be very effective in pollutant removal [13-14].

In this work, a lab-scale reactor was implemented to investigate the effectiveness of the continuous electrocoagulation process for boron removal from a high-concentration boron solution prepared synthetically. To this end, process optimization was attempted through testing the effect of different influent pH values and contact times.

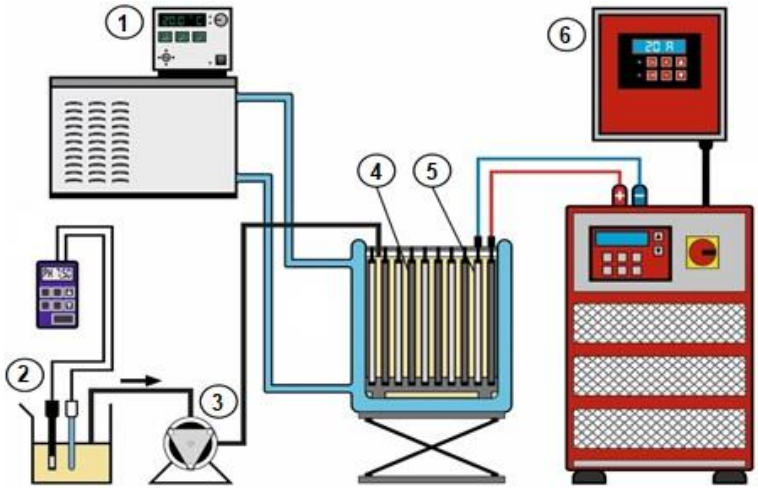
## 2. Materials and Methods

In this study, maintaining high boron concentration was decided to mimic boron industry wastewater. Synthetic wastewater samples were prepared for the experiments using borax (sodium tetraborate decahydrate: $Na_2B_4O_7$) from Merck with 99.99% purity. The boron solution of 1000 mg $L^{-1}$ was prepared by dissolving 4647.28 mg of borax dried at 105$^{o}$C in 1 L of distilled water.

A lab-scale plexiglass reactor (16 cm × 8 cm × 8 cm) was used for the experiments (Fig. 1). Two groups of aluminium electrodes, alternating between anodes and cathodes by eight plates of each type, were arranged vertically. The net spacing between the aluminium electrodes was 5 mm. They were connected to the terminals of a direct current (DC) power supply characterized by 0-10 A range for current and 0-30 V range

for voltage. At the beginning of each run, the prepared boron solution (i.e. 1000 mg $L^{-1}$) was fed into the reactor. The moment the DC power supply was switched on was considered as starting time for each run.

The analytical determination of boron in the samples was conducted potentiometrically by using mannitol ($C_6H_{14}O_6$), which forms a complex compound with $BH_3O_3$. For this purpose, boron analyses were carried out as follows: after filtering the samples, 5 g $C_6H_{14}O_6$ were added. The solution was then titrated with 0.5 N of potassium hydroxide (KOH) until the pH was adjusted to 7.6. The boron amount was calculated via the KOH consumption [9]. This method was selected to eliminate any potential aluminium interference in the boron detection that is likely in the case of spectrophotometric methods such as the Carmin, Azomethine-H and Curcumin methods [10].

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|---|---|
| **1:** Temperature control | **4:** Anode |
| **2:** pH meter | **5:** Cathode |
| **3:** Vacuum Pump | **6:** Direct current power supply |

**Figure 1.** Process diagram of the experimental system applied in this study for boron removal under different influent pH values and retention times.

## 3. Results

During the runs, the effect of parameters such as the influent pH as well as different electrocoagulation durations on boron removal were investigated after ensuring that current density and initial boron concentration were kept unchanged during all sets of experiments. Supporting electrolyte can be used in

similar experiments. Its conductivity impacts on the cell resistance. In addition, the electrolyte solution properties influence the interaction with the electroactive species, thus affecting the electrode reactions [15-16]. However, the investigation of the effect of this parameter was out of the scope of this work and, therefore, supporting electrolyte was not used in the current study.

### 3.1 Initial pH

The initial pH is amongst the most important factors affecting the performance of the electrocoagulation processes [16-17]. The aluminium hydroxide ($Al(OH)_3$) is amphoteric. Hence, the formation of the $Al(OH)_3$ flocs is significantly affected by the pH. Within a pH range of 4-9, aluminium hydroxides with positive charge (e.g. $Al(OH)^{2+}$, $Al(OH)_2^{+}$, $Al_2(OH)_2^{4+}$, $Al(OH)_3$, $Al_{13}(OH)_{32}^{7+}$) and high adsorption capacity are formed. As soon as the pH exceeds the value of 9, the dominant aluminium form is tetrahydroxyaluminate ion ($Al(OH)_4^{-}$) which, however, dissolves and does not form flocs [11, 16, 18].

In this study, the pH effect on boron removal through electrocoagulation was examined by conducting experiments at different influent pH values (i.e. 4, 5, 6, 7.45 and 9); current density was kept constant at 5 A and the electrocoagulation duration was 50 min. The results showed that boron removal increased from 57 to 67% with the pH increase from 4 to 6. On the contrary, further pH increase to 9 resulted in decreasing the boron removal 52% (Fig. 2). According to the obtained experimental results, optimum boron removal was achieved at pH=6. Solid $Al(OH)_3$ is the dominant form especially when the pH is between 6 and 7 [18-19]. It is likely that an initial pH equal to 6 provided the optimal conditions for boron precipitation through the formation of aluminium borate ($AlBO_3$).

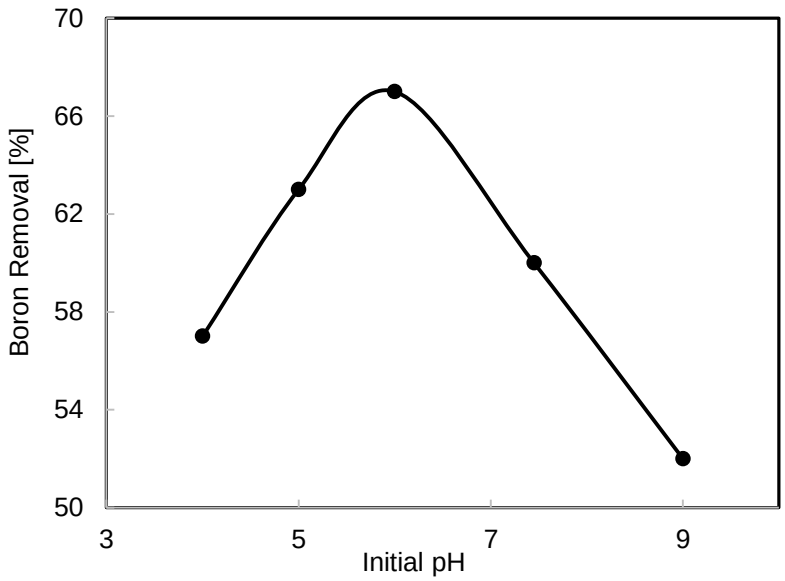

**Figure 2.** Effect of different influent pH values on boron removal. The current intensity was kept constant at 5 A and the electrocoagulation duration was 50 min.

In addition, the effect of different influent pH values on the effluent pH measured at the end of the reaction time (i.e. 50 min) is shown in Fig. 3. The pH increases whilst the electrocoagulation proceeds because of the hydrogen evolution at the cathode [16, 19]. The highest the influent pH, the highest the measured pH at the end of the electrocoagulation process.

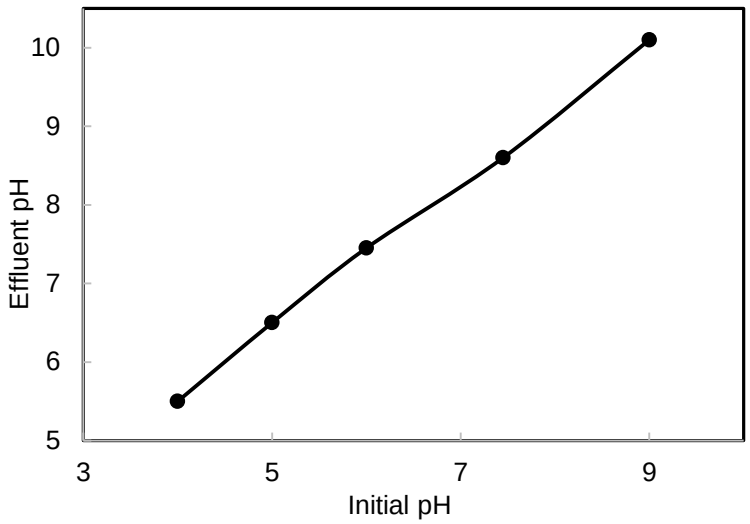


**Figure 3.** The change in the pH at the end of the electrocoagulation process for each of the different tested influent pH values. The current intensity was kept constant at 5 A and the electrocoagulation duration was 50 min.

### 3.2 Duration of electrocoagulation process

The decision upon the duration of the electrolysis is another important factor that determines the pollutants removal [12, 16]. While exploring the electrocagulation duration effect, the current density was kept constant at 5 A. The influent pH was adjusted to 6 according to the results of the previous section. As shown in Fig. 4, comparable changes in the boron removal were observed as the electrolysis time increased. Boron removal equal to 45, 53, 65 and 79% was measured for durations equal to 10, 25, 50 and 100 min, respectively. After 10 min of electrolysis, the removal efficiency was quite low (45%). Thus, an operation time of 10 min was found insufficient to achieve satisfying boron removal. Increasing the duration of the electrocoagulation process caused a considerable rise in the removal rates with the highest one (79%) occurring at the highest tested operation length (100 min).

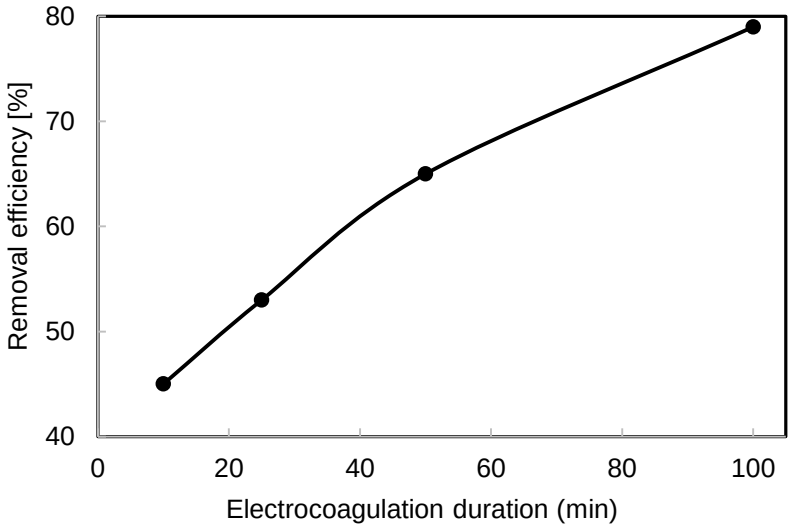


**Figure 4.** The effect of the duration of the electrocagulation process on boron removal. The current intensity was kept constant at 5 A and the influent pH was 6.

Providing more time for the electrocagulation process results in increasing the amount of the electro-generated $Al^{3+}$, thus leading to the production of a higher number of flocs comprised of insoluble monomeric and polymeric aluminium hydroxides. Moreover, it is translated into a longer contact time between the heavy metal ions and the flocs. Therefore, more heavy metal ions are removed through adsorption and co-precipitation with the flocs [12, 16].

## 4. Discussion

In the current study, boron removal from a boron-containing solution prepared synthetically was explored by employing the continuous electrocoagulation process with plate-type aluminium electrodes. The effect of changing operational variables (i.e. influent pH and retention time) on the process performance was examined. The current intensity was kept constant at 5 A throughout the study. With respect to the initial pH effect, various influent pH values were tested (4, 5, 6, 7.45 and 9) with the optimal boron removal (67%) occurring at pH=6. This result was supported by pH-related activity for aluminium hydroxides. At pH=6, $Al(OH)_3$ is the dominant aluminium hydroxide form, thus enhancing boron precipitation via $AlBO_3$ formation.

Moreover, increasing the electrocoagulation duration from 10 to 100 min was observed to increase boron removal from 45% to 79%. Under constant current density (5 A) and with the initial pH adjusted to 6,

extending the electrocoagulation process enabled higher anodic dissolution and, thus, higher coagulants release. The existence of more coagulants per unit of pollutants within the reactor led to increased boron removal.

This study showed that the continuous electrocoagulation process can constitute an appropriate treatment for boron removal after optimizing important operational parameters such as the initial pH and the process duration. Future work can focus on the optimization of other parameters such as current density and influent flow rate.

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