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The investigation of parameters affecting boron removal by electrocoagulation method

A. Erdem Yilmaz[a,∗], Recep Boncukcuoğlu[a], M. Muhtar Kocakerim[b], Bülent Keskinler[c]

[a] Department of Environmental Engineering, Atatürk University, Faculty of Engineering, Erzurum, Turkey
[b] Department of Chemical Engineering, 25240, Atatürk University, Faculty of Engineering Erzurum, Turkey
[c] Department of Environmental Engineering, Gebze Institute of Technology, Gebze/Kocaeli 41400, Turkey

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Abstract

Boron removal from wastewaters by electrocoagulation using aluminum electrode material was investigated in this paper. Several working parameters, such as pH, current density, boron concentration and type and concentration of supporting electrolyte were studied in an attempt to achieve a higher removal capacity. The experiments were carried out by keeping the pH of solution constant and optimum pH of solution was determined 8.0 for the aluminum electrode. Although energy consumption increased with decreasing boron concentration, which conductivity of these solutions were low, boron removal efficiency was higher at 100 mg/L than that of 1000 mg/L. Current density was an important parameter affecting removal efficiency. Boron removal efficiency and energy consumption increased with increasing current density from 1.2 to 6.0 mA/cm^2. The types of different supporting electrolyte were experimented in order to investigate to this parameter effect on boron removal. The highest boron removal efficiency, 97%, was found by $CaCl_2$. Added $CaCl_2$ increased more the conductivity of solution according to other supporting electrolytes, but decreased energy consumption. The results showed to have a high effectiveness of the electrocoagulation method in removing boron from aqueous solutions.

Keywords: Electrocoagulation; Boron removal; Aluminum electrode; pH; Wastewater treatment

1. Introduction

Boron is in a number of minerals, in nature, mostly calcium and/or sodium borates, such as colemanite ($2CaO{\cdot}3B_2O_3{\cdot}5H_2O$), ulexite ($Na_2O{\cdot}2CaO{\cdot}5B_2O_3{\cdot}16H_2O$) and tincal ($Na_2O{\cdot}2B_2O_3{\cdot}10H_2O$), etc. There is a variety of application including various boron fertilizers, insecticides, corrosion inhibitors in anti-freeze formulations for motor vehicle and other cooling system, 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 [1,2].

Boron is normally in very low amounts in soil and irrigation waters, but it 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, Ni, etc., and these complexes are more toxic than heavy metals forming them [3]. Although little amount of boron is a nutrient for some plants, its excessive amount affects badly the growth of many agricultural products. Also, the maximum boron level in drinking water for human health is given as 0.3 mg/L in WHO standards [3].

Because inorganic boron compounds are antiseptics, conventional biological treatment methods cannot be used for boron removal from wastewaters. Also, coagulation–precipitation methods are not effective and not feasible for this purpose. Also, ion exchange methods can be applied in boron removal from wastewater as an advanced

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[∗] Corresponding author. Tel.: +90 442 2314812; fax: +90 442 2360992.
E-mail addresses: aerdemy@atauni.edu.tr, aerdemy@yahoo.com (A.E. Yilmaz).

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method [4–7]. Unfortunately, this method is very expensive. So, electrocoagulation method is investigated as a new technology for boron removal.

Since boric acid and borates dissolve in water to form various borate ions, the composition of borate ions should be found out to understand the solution behavior, which depends on a number of factors, including the concentration of boron, the temperature and pH.

Electrocoagulation is a simple and efficient method where the flocculating agent is generated by electro-oxidation of a sacrificial anode, generally made of iron or aluminum. In this process, the treatment is done without adding any chemical coagulant or flocculants, thus forming the amount of sludge is reduced [8]. Electrocoagulation has been successfully used to treat oil wastes, with a removal efficiencies as high as 99% [9,10]. Similar successes were obtained when treating dye-containing solutions [11,12], potable water [13], urban and restaurant wastewater [14,15] and nitrate or fluoride containing waters [16,17]. In addition, a great deal of work performed in the last decades [18,19] has proved that electrocoagulation is an effective technology for the treatment of heavy metal containing wastewaters.

Electrocoagulation involves the generation of coagulants in situ by dissolving electrically either aluminum or iron ions from respectively aluminum or iron electrodes. The metal ion generation takes place at the anode; hydrogen gas is released from the cathode. Also, the hydrogen gas would help to float the flocculated particles out of the water. This process sometimes is called electrofloculation. The electrodes can be arranged in a mono- or bi-polar mode. The materials can be aluminum or iron in plate form or packed form of scraps such as steel turnings, millings, etc.

Electrocoagulation is a complex process occurring via serial steps such as electrolytic reactions at electrode surfaces, formation of coagulants in aqueous phase, adsorption of soluble or colloidal pollutants on coagulants which are removed by sedimentation or flotation.

The most widely used electrode materials in electrocoagulation process are aluminum and iron. In the case of aluminum, main reactions are as

$$\text{Anode}: \quad Al_{(s)} \rightarrow Al_{(aq)}{}^{3+} + 3e^- \tag{1}$$

$$\text{Cathode}: \quad 3H_2O + 3e^- \rightarrow 3/2H_{2(g)} + 3OH_{(aq)}{}^- \tag{2}$$

On the other hand, at high pH values, both cathode and anode may be chemically attacked by OH^- ions [20]:

$$2Al_{(s)} + 6H_2O + 2OH_{(aq)}{}^- \rightarrow 2Al(OH)_4{}^-{}_{(aq)} + 3H_{2(g)} \tag{3}$$

Al^{3+} and OH^- ions generated by electrode reactions (1) and (2) react to form various monomeric species such as $Al(OH)^{2+}$, $Al(OH)_2{}^+$, $Al_2(OH)_2{}^{2+}$, $Al(OH)_4{}^-$, and polymeric species such as $Al_6(OH)_{15}{}^{3+}$, $Al_7(OH)_{17}{}^{4+}$, $Al_8(OH)_{20}{}^{4+}$, $Al_{13}O_4(OH)_{24}{}^{7+}$, $Al_{13}(OH)_{34}{}^{5+}$, which transform finally into $Al(OH)_{3(s)}$ according to complex precipitation kinetics [21,22].

$$Al_{(aq)}{}^{3+} + 3H_2O \rightarrow Al(OH)_{3(s)} + 3H_{(aq)}{}^+ \tag{4}$$

Freshly formed amorphous $Al(OH)_{3(s)}$ "sweep flocs" have large surface areas which is beneficial for a rapid adsorption of soluble organic compounds and trapping of colloidal particles. Finally, these flocs are removed easily from aqueous medium by sedimentation or H_2 flotation.

The aim of this paper was to study the feasibility of the removal of boron from aqueous solution by electrocoagulation. The process was examined under different values of current density (CD), pH, initial boron concentrations, and type and concentration of supporting electrolyte, in order to determine optimum operating conditions.

2. Experimental

In this study, boron concentration was chosen high because boron concentration from boron industry wastewater was quite high. Wastewater samples used in the experiments were prepared synthetically using $Na_2B_4O_7$ having 99.99 of purity from Merck. The solution with boron concentration of 100 mg/L was prepared by dissolved 459.1 mg borax dried at 105 °C in distilled water and completed with distilled water to 1 L. The same operations were repeated for the solutions with boron concentrations of 250, 500 and 1000 mg/L with different $Na_2B_4O_7$ weights. The parameters chosen in the experiments carried out at 25 °C were pH, boron concentration, current density and type and concentration of supporting electrolyte, whose ranges were given in Table 1.

A laboratory-scale reactor (16 cm × 8 cm × 8 cm), made of plexiglass, was used in all experiments (Fig. 1). Two groups of alternating electrodes being cathodes and anodes (by eight plates of each type) made of aluminum were arranged vertically. The net spacing between the aluminum electrodes was 5 mm. They were connected to terminals of a direct current power supply characterized by the ranges 0–5 A for current and 0–30 V for voltage. At the beginning of each run the solution of boron of the desired concentration fed into the reactor. Each run was timed starting with the dc power supply switching on.

The analytical determination of boron was done potentiometrically by means of mannitol, which forms a complex compound with boric acid. For this purpose, boron analy-

Table 1
Experimental parameters

Parameters	Range
pH	5.0, 6.0, 7.0, 8.0 and 9.0
Current density (mA/cm^2)	1.2, 2.4, 3.6, 4.8 and 6.0
Boron concentration (mg/L)	100, 250, 500 and 1000
Type of supporting electrolyte	$CaCl_2$, NaCl, Na_2SO_4 and KCl
Concentration of supporting electrolyte (mM)	5, 10 and 15

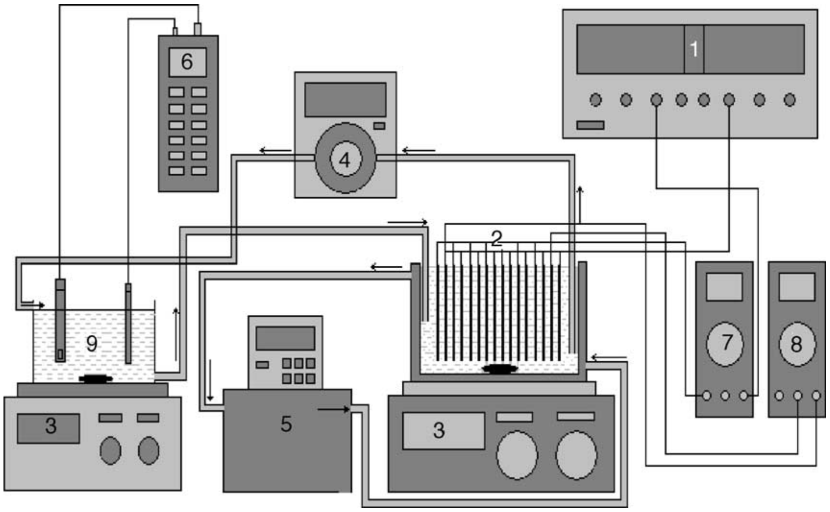

Fig. 1. Schematic view of the experimental system ((1) dc power supply, (2) electrocoagulation cell, (3) magnetic stirrer, (4) pump, (5) circulator, (6) pH and conductivity meter, (7) ampermeter, (8) voltmeter and (9) pH control unit).

ses were carried out following: Solution pH was adjusted to 7.60 after sample was filtered. Then, 5 g mannitol was added to solution. The solution was titrated with 0.5N KOH until solution pH became 7.60. Boron amount was calculated from KOH consumption. 1 ml 0.5N KOH is equal to 17.41 mg B_2O_3 [23]. This method was selected in order to prevent aluminum interference in boron detection done by spectrophotometric methods such as Carmin, Azomethine-H and Curcumin methods [24].

3. Results and discussion

3.1. The effects of parameters

In the runs, the effects of parameters such as pH, current density, boron concentration, type of supporting electrolyte and concentration of supporting electrolyte under the conditions which the reaction time hold in constant were investigated.

1. The effect of pH: It has been established that the pH has a considerable influence on the performance of electrocoagulation process. To evaluate this effect, a series of experiments were performed, using solution containing boron of 100 mg/L. The effect of pH on the boron removal was examined at 5.0, 6.0, 7.0, 8.0, and 9.0 pH. Current density of 3.0 mA/cm^2 and stirring speed of 150 rpm were kept constant in the experiments. Boron removal increased with increasing the pH up to 8.0, and then decreased. Increasing boron removal was the same tendency for all boron concentrations at pH 8.0. On the other hand, energy consumption increased with increasing the pH values. This is because the solution with the lowest pH value has the highest conductivity. When experiments were done without controlling pH at the beginning, pH increased very faster and reached to 10.0 and boron removal efficiency was quite low. The results obtained are shown graphically in Fig. 2a. If activity-pH diagram for Al(III) species in equilibrium with $Al(OH)_3$ is investigated, it will be seen that dominant Al(III) species is $Al(OH)_4^-$ at pH 9.0. $Al(OH)_4^-$ is a dissolving form and does not form flocs [25]. Experiments were carried at pH 5–9 because $Al(OH)_3$ formed at this pH interval, according to activity-pH diagram for Al(III) species. The pH was kept nearly constant throughout the experiments by adding (w/w 63%) concentrated HNO_3. Maximum 3–4 ml concentrated HNO_3 was added to solution for constant pH during experiment period. According to following reaction, HNO_3 kept nearly constant pH via neutralization:

$$OH^- + HNO_3 \rightarrow H_2O + NO_3^- \tag{5}$$

At these conditions, nitrate ion was not expected to be effect on boron removal. As a result of obtained data, optimum boron removal was reached at pH 8.0. This is probably resulting from borate and Al(III) species which form in solution at this pH. The results obtained are shown graphically in Fig. 2b and c for 100 mg/L boron concentration.
2. The effect of current density: The current density determines the coagulant dosage rate. Thus, this parameter should have a significant impact on removal efficiencies of pollutants. To investigate the effect of current density on the boron removal, a series of experiments were carried out by solutions containing a constant pollutants loading with current density being varied from 1.2 to 6.0 mA/cm^2. The 8.0 of solution of pH and stirring speed of 150 rpm were kept constant and boron concentrations were taken 100, 250, 500 and 1000 mg/L in experiments. Dissolving rate of Al electrode increased with increasing current density. Consequently, boron removal increased with increasing current density because more Al^{3+} passed to solution at higher current density and formation

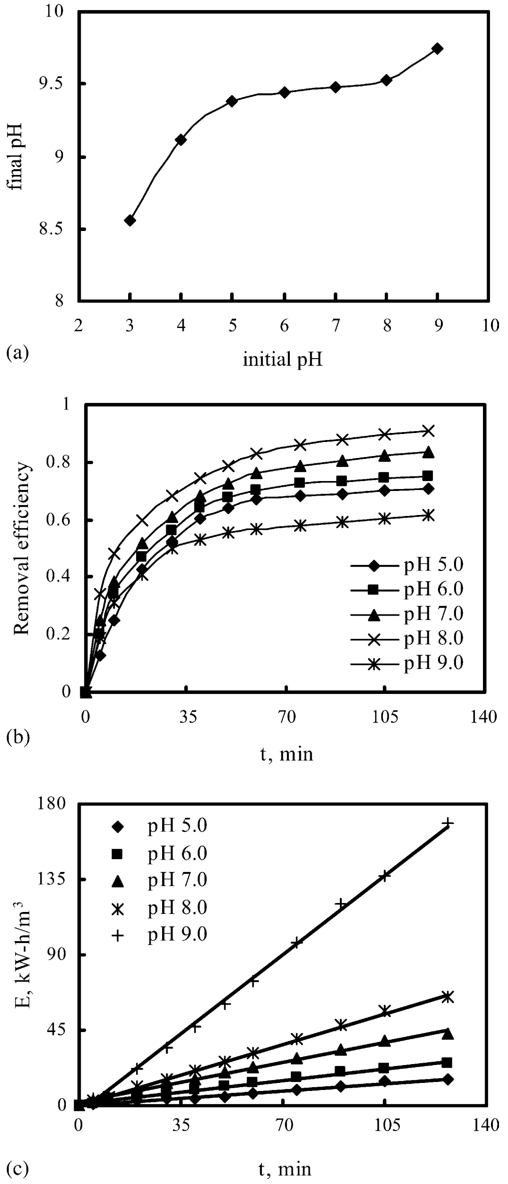

Fig. 2. (a) pH variation after electrocoagulation (current density: 3.0 mA/cm^2, initial boron concentration: 100 mg/L and stirring speed: 150 rpm). (b) The effect of pH on the boron removal (current density: 3.0 mA/cm^2, initial boron concentration: 100 mg/L and stirring speed: 150 rpm). (c) The effect of pH on the energy consumption (current density: 3.0 mA/cm^2, initial boron concentration: 100 mg/L and stirring speed: 150 rpm).

rate of Al(OH)$_3$ increased. As a result of increasing current density, applied potential increased. Thus, energy consumption increased with increasing potential. When current density was increased from 1.2 to 6.0 mA/cm^2 for solution including 100 mg/L boron, energy consumption reached from 6.33 to 141.33 kW h/m^3. The results obtained were shown graphically in Fig. 3a and b for 100 mg/L boron concentration.

3. The effect of initial boron concentration: The effect of initial boron concentration on the boron removal was examined with solutions including boron of 100, 250, 500 and 1000 mg/L. Current density of 3.0 mA/cm^2, optimum pH of 8.0 and stirring speed of 150 rpm were kept constant in the experiments. The solution conductivity increased with increasing boron concentration. As a result of this situation, applied potential and energy consumption decreased. On the contrary, boron removal efficiency decreased with increasing boron concentration. This can be explained as following; although the same amount Al^{3+} passed to solution at the same current density for all boron concentration, Al^{3+} was insufficient for solutions including higher boron concentration. Because of increasing boron concentration, potential applied to solution and energy consumption decreased. The results obtained were shown graphically in Fig. 4a and b.

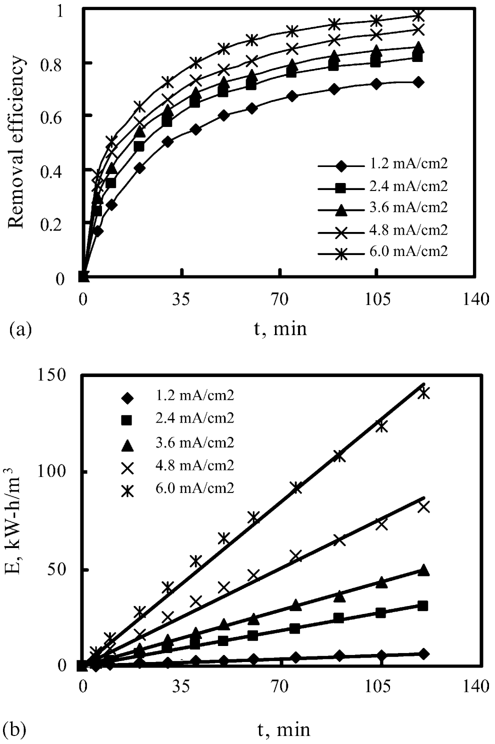

Fig. 3. (a) The effect of current density on the boron removal (initial boron concentration: 100 mg/L, pH 8.0 and stirring speed: 150 rpm). (b) The effect of current density on the energy consumption (initial boron concentration: 100 mg/L, pH 8.0 and stirring speed: 150 rpm).

4. The effect of type of supporting electrolyte: The effect of type of supporting electrolyte on the boron removal was examined with 15 mM NaCl, 15 mM KCl, 10 mM Na$_2$SO$_4$ and 10 mM CaCl$_2$. Current density of 3.0 mA/cm^2, stirring speed of 150 rpm and optimum pH of 8.0 were kept constant in the experiments. All supporting electrolyte were examined for boron concentration of 100, 250, 500 and 1000 mg/L. Although boron removal increased with all supporting electrolyte type, the highest boron removal was observed with 10 mM CaCl$_2$. The results obtained were shown graphically in Fig. 5a and b for 100 mg/L boron concentration.

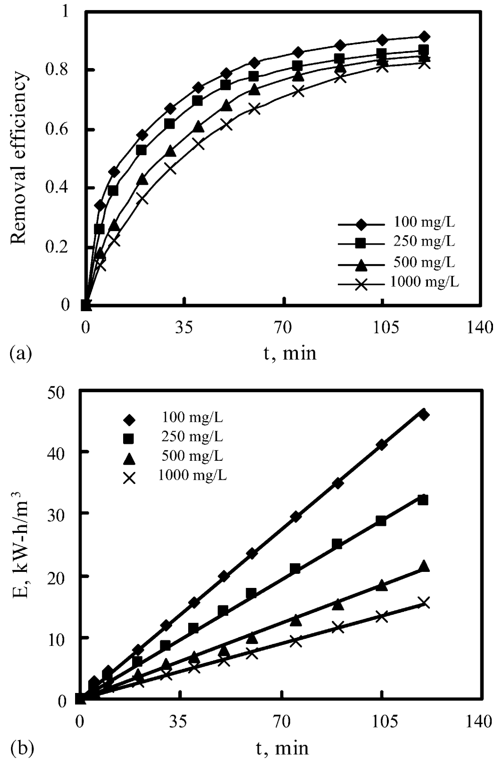

Fig. 4. (a) The effect of initial boron concentration on the boron removal (current density: 3.0 mA/cm^2, pH 8.0 and stirring speed: 150 rpm). (b) The effect of initial boron concentration on the energy consumption (current density: 3.0 mA/cm^2, pH 8.0 and stirring speed: 150 rpm).

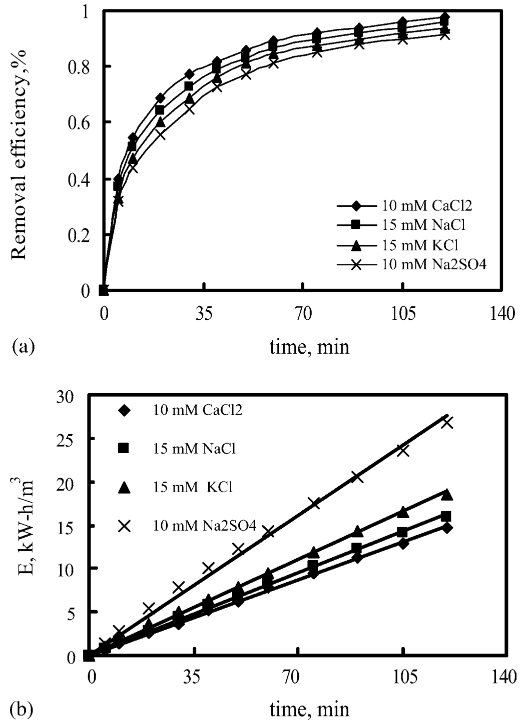

Fig. 5. (a) The effect of type of supporting electrolyte on the boron removal (initial boron concentration: 100 mg/L, current density: 3.0 mA/cm^2, pH 8.0 and stirring speed: 150 rpm). (b) The effect of type of supporting electrolyte on the energy consumption (initial boron concentration: 100 mg/L (current density: 3.0 mA/cm^2, pH 8.0 and stirring speed: 150 rpm).

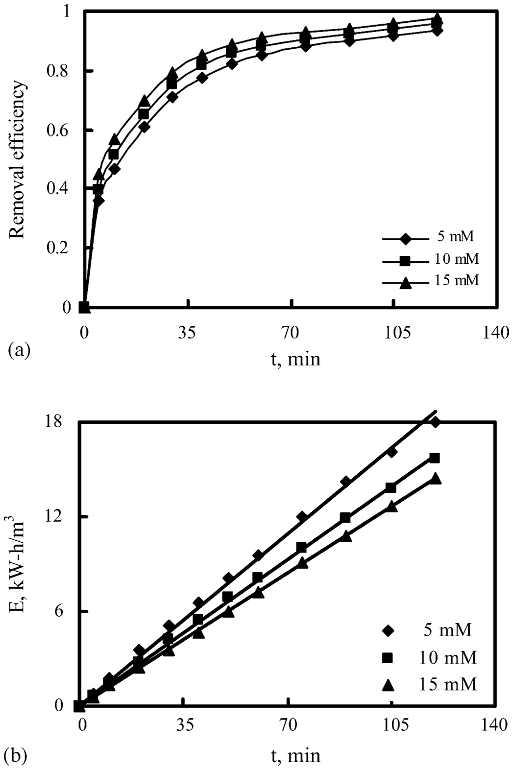

Fig. 6. (a) The effect of concentration for $CaCl_2$ supporting electrolyte on the boron removal (initial boron concentration: 100 mg/L, current density: 3.0 mA/cm^2, pH 8.0 and stirring speed: 150 rpm). (b) The effect of concentration for $CaCl_2$ supporting electrolyte on the energy consumption (initial boron concentration: 100 mg/L, current density: 3.0 mA/cm^2, pH 8.0 and stirring speed: 150 rpm).

5. The effect of concentration of supporting electrolyte: The effect of concentration of supporting electrolyte on the boron removal was examined with 5, 10 and 15 mM $CaCl_2$. Current density of 3.0 mA/cm^2, optimum pH of 8.0 and stirring speed of 150 rpm were kept constant in the experiments. All concentration of supporting electrolyte was examined for boron concentration of 100 mg/L. As expected, the obtained results showed that boron removal increased with increasing concentration of supporting electrolyte. In addition, the energy consumption decreased with increasing concentration of supporting electrolyte because potential decreased under constant current density. The results obtained were shown graphically in Fig. 6a and b for 100 mg/L boron concentration.

4. Conclusion

The results of this study showed that electrocoagulation could be applied in the treatment of industrial wastewater containing boron. The use of aluminum as sacrificial electrode material in the treatment of boron wastewater by electrocoagulation was found to be pH dependent. The most effective removal capacity was achieved at the pH 8. Although increasing boron concentration decreased boron removal efficiency, this increase decreased energy consumption. The treatment rate was seen to increase with increasing the current density. The highest current density obtained the quickest treatment for boron removal from industrial wastewaters.

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