Evaluation of Boron Removal by Coagulation-Flocculation and Electrocoagulation

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Abstract - **High boron levels in drinking water can be toxic to humans. According to the WHO regulations (2011), the boron concentration should be reduced to less than 2.4 mg L^{-1} for drinking water. The aim of this study is to investigate the feasibility of coagulation-flocculation and electrocoagulation as a pre-treatment process to remove boron from natural water. Standard jar tests using coagulation and flocculation simulator were carried out to determine the effectiveness of chemical pre-treatment for removal of boron. (MgCl$_2$, 6H$_2$O) was used as coagulation adjuvant in combination with optimum coagulant dose to observe their differential effects. To optimize the experimental conditions of boron removal, commercial flocculant was used. Afterward the performance of electrocoagulation process to remove boron was investigated by optimizing the experimental conditions, such as pHi, electrolysis time, initial conductivity of the solution (i), and current density. Experiments were carried out with initial boron concentration of 5 mg L^{-1}.**

Keywords— Coagulation; alum; electrocoagulation; aluminium electrode; Boron removal;

I.   INTRODUCTION

Desalination of seawater and brackish water has become increasingly important as a source of water supply to contend with the population burden worldwide. The occurrence of boron which exists mainly in the form of boric acid (H$_3$BO$_3$) in water is undesirable. Boron is one of the inorganic constituents that are problematic and difficult to get rid of. The presence of boron in water has two differentiated origins, one of which is natural origin due to the boron in silts present in the aquifer and the other one is the anthropogenic origin, such as wastewater discharge from boron mines and boric acid plants. In order to prevent the environmental problems of high concentration of boron in waters, their boron contents should be removed by a suitable method [1].

Boron is widely distributed in the environment, from natural or anthropogenic sources. It can be found mainly in the form of boric acid or borate salts. When the acid dissociation constant of boric acid (5.81×10^{-10} at 25°C; pKa = 9.24) is considered, it can be predicted that H$_3$BO$_3$ is the predominant form at neutral and low pHs whereas BO$_3^{3-}$ is expected to be present at high pHs. Both forms may exist in equilibrium at a pH range of 7.0–11.5. At physiological pHs, the undissociated form, H$_3$BO$_3$, is predominant.

Boron is an important micronutrient for plants, animals and humans, but it can be toxic at high concentrations. In recent years the use of boron compounds in metallurgy, microelectronics, glass products and in fertilizers has been increasing; so that boron compounds are released into the environment from these sources [2].

High levels of boron are found in seawater (4.7 mg L^{-1}), domestic wastewater (0.5–2 mg L^{-1}), and regional groundwater (e.g., Italy Cyprus and Greece with boron content up to 8 mg L^{-1}). High boron levels in drinking water can be toxic to humans as boron has been shown to cause male reproductive impediments in laboratory animals [3]. The World Health Organization for many years had recommended the drinking water limits for boron as low as 0.5 mg L^{-1}. Lately, the Expert Group on Guidelines for Desalination recommended that the guideline for boron should be reconsidered in the light of new thinking on the toxicity, as boron levels are quite high in seawater and boron removal is difficult [4, 5]. Therefore, the Drinking Water Quality Committee, at its meeting of 9-13 November 2009, recommended revising the Boron Guideline Value to 2.4 mg L^{-1}. The revised Guideline Value was incorporated into the Guidelines for Drinking-Water Quality, 4th Edition, that was published in 2011 [5, 6].

In areas where the shortage of water is a concern, processes have been developed to obtain water from seawater and brackish waters by means of reverse osmosis (RO) processes. These processes present percentages of elimination of salts superior in most cases to 98%. Therefore, Marifias [7] reports the use of RO to eliminate boron, always at high pH, assure that the chemical form of the boron is of borates, presenting, due to the pH, the problem of the deposition on the membranes of other compounds (mainly salts of calcium and magnesium) that involve frequent chemical cleaning.

Chemical coagulation followed by sedimentation is a proven technique for the treatment of high suspended solids wastewater especially those formed by the colloidal matters. Research and practical applications have shown that coagulation will lower the pollution load and could generate an adequate water recovery [8–10]. Coagulation is mainly done with inorganic metal salts, e.g. aluminum and ferric sulfates and chlorides which are widely used as coagulants in water and wastewater treatment and in some other applications. Electrochemical technology contributes in many ways to a cleaner environment and covers a very broad range of technology [5, 11, 12]. Electrocoagulation (EC) is an efficient method used for treating various process effluents and investigated as a new technology for boron [5, 12, 13].

The aim of this study is to investigate the feasibility of coagulation-flocculation and electrocoagulation as pre-treatment processes for boron removal.

II. MATERIALS AND METHODS

A. Jar tests

A standard jar test apparatus, Four-Paddle Stirrer with illuminated base was employed for the tests. An illuminated base helps observation of the floc formation and settling characteristics.

The Jar Test apparatus was programmed with the desired experimental procedure. The coagulant/ coagulant aid solutions were prepared by dissolving required amount of chemicals. A 500 mL measuring cylinder was used to transfer 500 mL of solution into each of the four 1L jars. Desired quantities of coagulant were pipette into each jar. The jars were then positioned in the apparatus and the program started. Each jar was rapid mixed at 250 round per minute (rpm) for 2 minutes. Coagulant was added towards the end of this period. Stirring speed was reduced to 50 rpm for 20 minutes, to allow flocculation to occur. Stirring was stopped and the sample was allowed to settle for 60 minutes. Samples of supernatant from each beaker were taken and filtered.

B. Electrocoagulation tests

The electrolytic cell used to conduct the experiments consists of a 1 L glass beaker. Electrocoagulation tests were performed in the electrolytic cell with two opposing aluminum plates served as parallel–vertical electrodes. For each electrode, the immerged active surface was 30 cm^2 (6 cm × 5 cm). The anode/cathode gap was kept constant at 2.5 cm. The electrodes assembly was connected to DC power supply providing current and voltage in the range of 0 - 5 A and 0 - 18 V. A gentle magnetic stirring rate of about 300 rpm was applied to the electrolyte in all tests.

C. Chemical analysis

The boron analysis method that has been used was molecular absorption spectrometry in the UV–visible range using Azomethine-H as a colorimetric reagent according to the procedure of López et al. [14]. Azomethine-H is not considered as a standardised reagent for boron analysis in waters. However, it has been selected owing to its simplicity and competitiveness over other Spectrophotometric reagents, according to Fuente and Munoz [15].

The performance was measured in terms of removal efficiency (% removal). The mathematical expression for their calculation was:

$$\% \ removal = \frac{(C_i - C_f)}{C_i} \times 100 \qquad (1)$$

where: C_i = initial boron concentration (mg L^{-1}) and C_f = residual boron concentration (mg L^{-1})

III. RESULTS AND DISCUSSION

A. Boron removal by coagulation flocculation

1) Effect of coagulant dose.

To determine the optimum coagulant dose for boron removal with alum, different jar tests were carried out for an initial boron concentration of 5 mg L^{-1} with increasing amounts of coagulant, starting with 20 mg L^{-1} up to 60 mg L^{-1}.

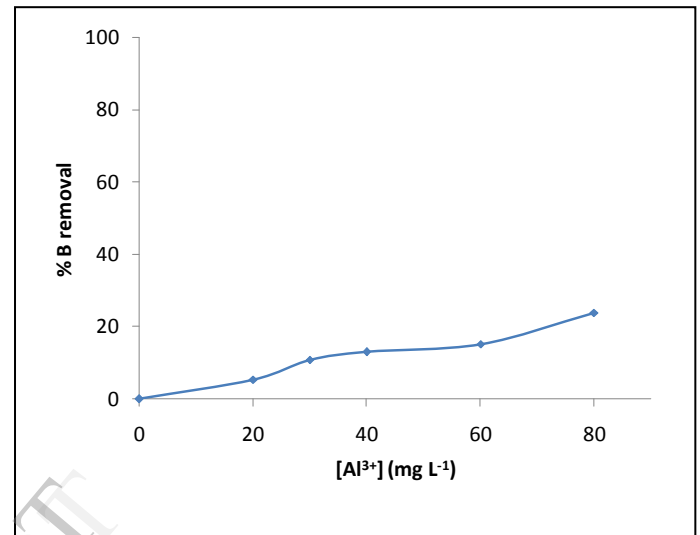The obtained results are shown in Fig. 1

Fig .1. Effect of coagulant dosage on boron removal

The alum coagulation and flocculation efficiency was slightly improved with the increasing of coagulant dose. The obtained results allow us to choose an optimal dose of coagulant of 30 mg L^{-1} corresponding to a restricted boron removal of about 10%.

2) Effect of coagulation adjuvant dose

The effect of magnesium chloride ($MgCl_2$, $6H_2O$) as coagulation adjuvant on boron removal was investigated for an initial boron concentration of 5 mg L^{-1}. Different coagulation tests were carried out by combining the optimal dose of coagulant with increasing adjuvant dose starting with 250 mg L^{-1} up to 1500 mg L^{-1}.

Fig. 2. depicts the evolution of boron removal as function of $MgCl_2$,$6H_2O$ dose. The uptake of boron as a function of coagulation adjuvant dose showed that adding $MgCl_2$,$6H_2O$ did not enhanced boron removal by Alum coagulation.
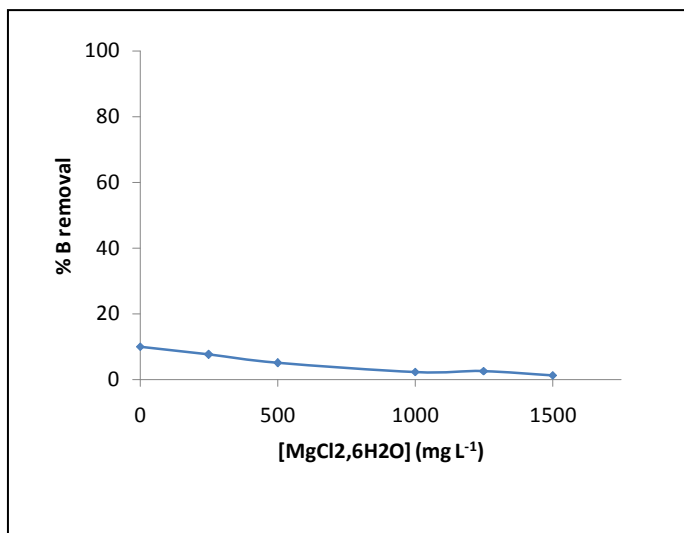
Fig. 2. Variation of boron removal as a function of coagulation adjuvant dose

3) Optimization of the flocculent dose

To optimize the experimental conditions of boron removal, commercial flocculent (anionic) was used in combination with optimum precipitant and coagulant doses to observe its effect. Different jar tests were carried out with increasing amounts of flocculent starting with 0.6 mg L^{-1} and increasing this by 0.6 mg L^{-1} increments up to 4.2 mg L^{-1}. The results obtained (not shown) reveal that boron removal did not change significantly with increasing doses of flocculent. It seems that flocculent addition leads to thickly developed flocs which are more settlebale and filtrable.

B. Boron removal by electrocoagulation

Operating parameters such as initial pH, current density, eletrolysis time and conductivity of the solution (σi) were optimized for an initial boron concentration of 5 mg L^{-1}.

1) Effect of initial pH.

The pH of solution plays an important role in EC process [16]. To investigate this effect, a series of experiments were carried out at pH 5–10 interval. The variation of pH after EC was determined. As seen from Fig. 3, the final pH value increases up to 8.6–9.1 when the initial pH = 4–9. However, for pH_i = 10, the pH_f decrease to 9.1. The use of soluble anodes causes the pH increase in the solution, for the reason of amorphism of aluminum hydroxide that is being form in the process of electrolysis [17].

In EC process, the evolution of H_2 at the cathode will increase the OH^- concentration. Thus, pH in the aqueous solution will increase when the pH of original water is in the range of 4–9. However, when the pH of the original water is higher than 9, the pH of the treated water will decrease. EC can neutralize the pH of the treated water to some extent via following reactions.

Under acid conditions, CO_2 can be purged with the evolution of H_2 and O_2. Particularly, Al dissolution and the formed $Al(OH)_3$ also dissolve, are responsible for the increase of solution's pH. At high pH, the formation of $Al(OH)_3$ near

the anode would release H^+ leading to decrease of pH. These processes are responsible for the decrease of aqueous pH [5, 18].

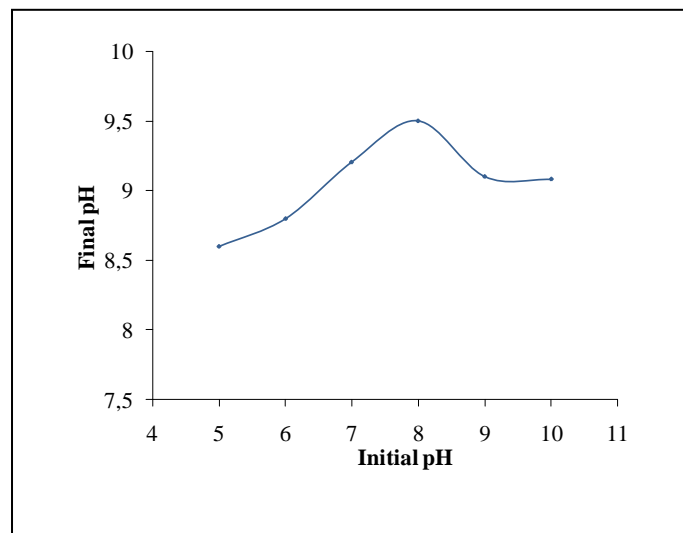Fig. 3. Evolution of final pH vs. initial pH
(J =15 mA cm^{-2}; t_{EC} = 90 min and σ_i = 29 mS cm^{-1})

On the other hand, it has been established that the pH has a considerable influence on the performance of EC process. Fig. 4 shows the effect of pH on the boron removal, it was observed that boron removal increased with increasing the pH up to 8.0, and then decreased. Boron removal was found to have the same tendency for all boron concentrations at pH 8.0. [1, 13, 19]
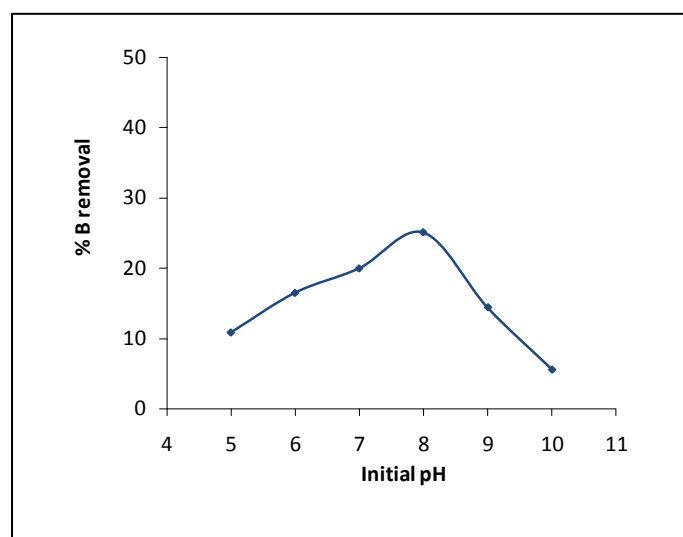

Fig. 4. Effect of initial pH on boron removal,
(J = 15 mA cm^{-2}; t_{EC} = 90 min and σ_i = 29 mS cm^{-1})

If activity–pH diagram for Al (III) species in equilibrium with $Al(OH)_{3s}$ is investigated, it will be seen that dominant Al (III) species is in the form of $Al(OH)_{3s}$ at pH 5.0–8.5 interval. $Al(OH)_4^-_{aq}$ forms at the higher pH is a dissolving form and does not form flocks [20].

When effect of pH on boron removal was investigated, borate ions species presented in solution must be known. For solution pH higher than pH 9.0, borate ions in solution was dominantly $B(OH)_{4\ aq}^-$ form. When solution pH was lower than pH 9.0, borate ions in solution was dominantly $B(OH)_3$ form. The highest boron removal efficiency was obtained at pH 8.0 because boron was at $B(OH)_3$ form and the formation $Al(OH)_{3s}$ was a quite high at this pH [5, 21].

The boron removal reached 25 % at initial pH of 8.0. Similar removal efficiencies were found by several authors [1, 5, 13, 19, 22]. Therefore, all EC experiments were conducted at $pH_i = 8$.

2) Effect of current density and EC time

Operating current density is very important in EC process because it is the only operational parameter that can be controlled directly. The current density determines the coagulant dosage rate. Thus, this parameter should have a significant impact on removal efficiencies of pollutants [18].

In an electrochemical process, the most important economical parameters is energy consumption W (kWh m^{-3}). This parameter is calculated from the following expression:

$$W = \frac{U.I.t_{EC}}{V} \qquad (2)$$

where U is the applied tension (V), I is the current intensity (A), t_{EC} is the time of EC (s) and V is the volume (m3) of boron solution.

The effect of current density on boron removal and energy consumption was investigated for current density varing from 24.8 to 157.9 mA cm^{-2}. The results obtained are shown graphically in Fig. 5. and Fig. 6.
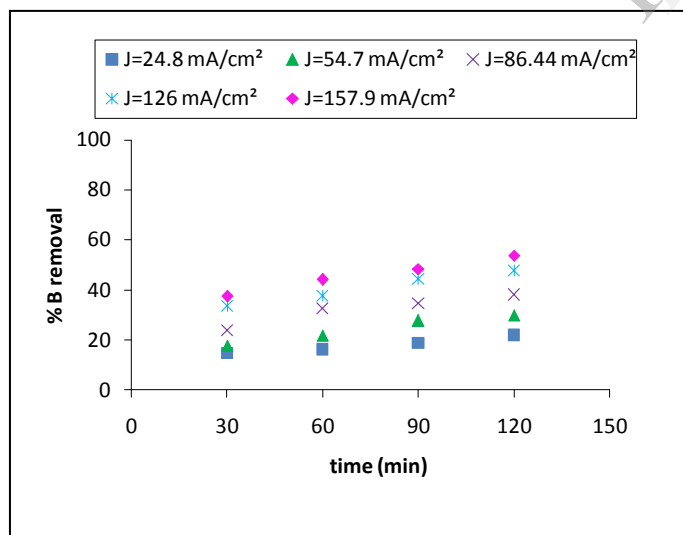

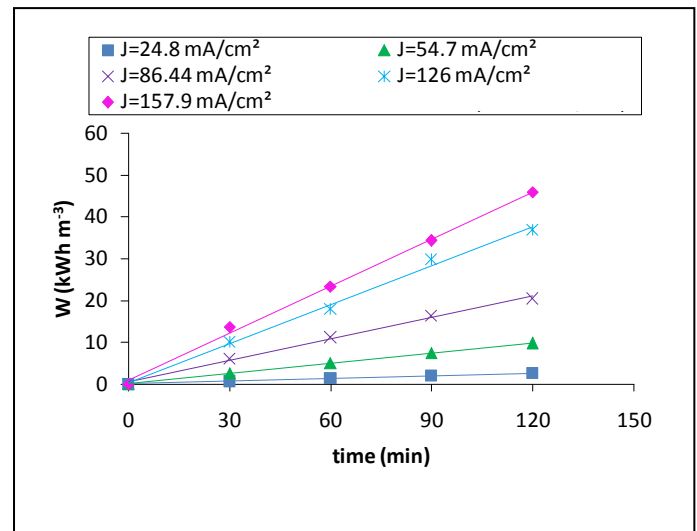Fig. 5. Effect of current density and EC time on boron removal %B, (pH = 8 and σ_i = 29 mS cm^{-1})

Fig. 6. Effect of current density and EC time on energy consumption, (pH = 8 and σ_i = 29 mS cm^{-1})

Fig. 5 shows that boron removal efficiency increased with increasing of current density and EC time. Also obtained results displayed that an increase of current density notably reduces the treatment duration. The highest current (157.9 mA cm^{-2}) produced the quickest removal rate, with a removal of 54 % for a treatment time of 120 min. This expected behavior is easily explained by the increase of coagulant and bubbles generation rate, resulting in a more efficient and faster removal, when the current is increased [10]

Dissolving rate of Al electrode increased with increasing current density. Consequently, boron removal increased with increasing current density because of a better chemical dissolution and formation rate of $Al(OH)_3$.

Increase of current density and time results in both enhancement of boron removal and considerable increase of energy consumption. Thus, to choose the optimal current density and the optimal EC time, conciliation should be done between economically appropriate energy consumption and acceptable boron removal efficiency. Therefore J = 86.44 mA cm^{-2} and t_{EC} = 60 min were fixed as optimal conditions.

3) Effect of initial conductivity

When the electrolytic conductivity is low, the current efficiency will decrease. And, high-applied bias potential is needed which will lead to the passivation of electrode and increase treatment cost. Generally, NaCl was added in order to increase the electrolytic conductivity [18].

The addition of Cl$^-$ will also decrease the negative effect of CO_3^{2-} and SO_4^{2-}. The presence of CO_3^{2-} and SO_4^{2-} will lead to the deposition of Ca^{2+} and Mg^{2+} and formation of oxide layer, which will decrease the current efficiency rapidly. It is therefore recommended that among the anions present, there should be 20% Cl$^-$ to ensure a normal operation of EC in water treatment [18].

To highlight the effect of initial conductivity on the boron removal a series of electrocoagulation tests were performed by varying the initial conductivity in the range of 28.5 - 52 mS cm^{-1}.
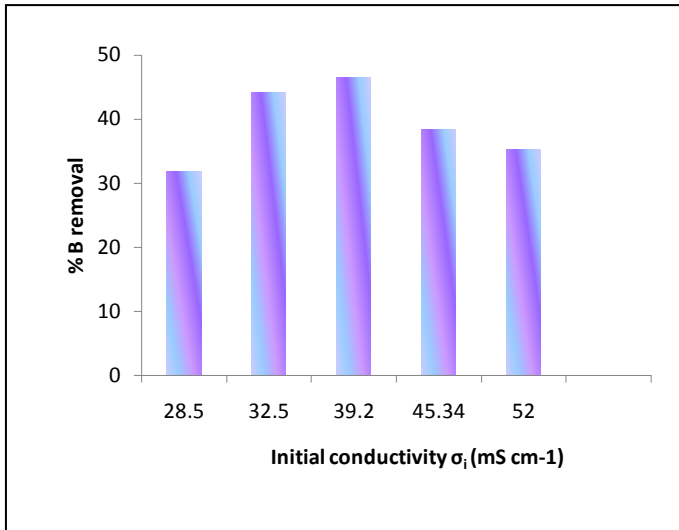
Fig. 7. Effect of initial conductivity on boron removal, (pH = 8 ; J = 86.44 mA cm^{-2} and t$_{EC}$ = 60 min)
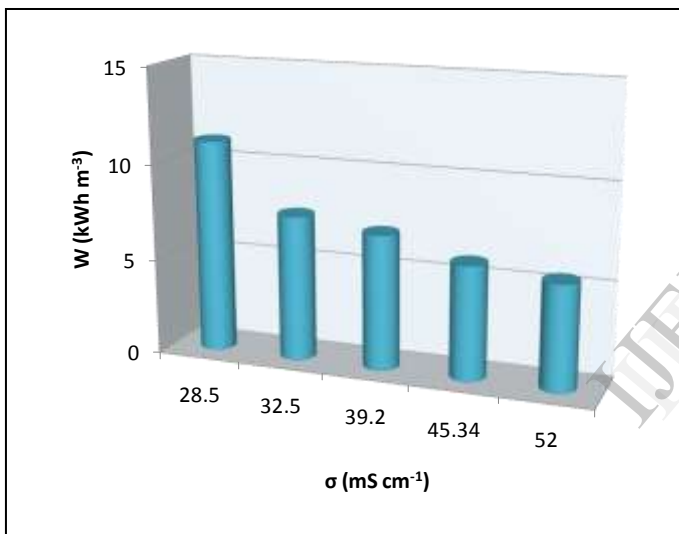

Fig. 8. Effect of initial conductivity on energy consumption, (pH = 8 ; J = 86.44 mA cm^{-2} and t$_{EC}$ = 60 min)

From Fig.7 experimental results showed that for initial conductivity values under 39 mS cm^{-1}, boron removal increased with the initial conductivity. Upper values of conductivity attenuated the boron removal efficiency. The effect of initial conductivity on the energy consumption was evaluated. The results obtained are shown graphically in Fig. 8.

The addition of NaCl would also lead to the decrease in power consumption because of the increase in conductivity. Our results confirmed that high conductivity values result in low energy consumption under the same current density. This could be attributed to solution resistance decrease.

IV. CONCLUSION

Coagulation flocculation with alum was not able to remove more than10 % of boron and was not able to meet the drinking water standard of 2.4 mg L^{-1}.

When considering boron removal by electrocoagulation, the removal is rapid at higher current densities. Conciliation must be found between economically suitable energy and removal efficiency.

A boron removal of 33 % could be reached for a current density of J = 86.44 mA cm^{-2} and electrolysis time of t = 60 minutes . These optimal conditions results in an energy consumption of 11.1 kWh m^{-3} for an initial boron concentration of 5 mg L^{-1}. Electrocoagulation could be used to reduce boron amount from water but to reach the drinking water standard, higher current density en treatment time must be applied.

An investigation effort remains to be done to improve the boron removal efficiency by EC. The treatment performance for aluminum electrodes could be enhanced by optimizing the EC unit and studying the effect of several other parameters.

REFERENCES

1. A. Erdem Yilmaz , Recep Boncukcuoğlu , M. Muhtar Kocakerim, "A quantitative comparison between electrocoagulation and chemical coagulation for boron removal from boron-containing solution" , J. Hazard. Mater., 149, 2007, pp. 475–481
2. Ö. Kaftan, M. Açıkel , A. E. Eroğlu, T. Shahwan , L. Artok , C. Ni, "Synthesis, characterization and application of a novel sorbent, glucamine-modified MCM-41, for the removal/preconcentration of boron from waters", Anal. Chim. Acta, 547, 2005, pp. 31–41
3. W. Bouguerra, A. Mnif , B. Hamrouni, M. Dhahbi, "Boron removal by adsorption onto activated alumina and by reverse osmosis", Desalination 223, 2008, pp. 31–37
4. WHO, Boron in Drinking-Water, Background Document for Preparation of WHO Guidelines for Drinking-Water Quality. Geneva, World Health ORGANIZATION," 2003, pp. 1-10
5. K. Missaoui, W. Bouguerra, C. Hannachi, B. Hamrouni, "Boron Removal by Electrocoagulation   Using Full Factorial Design", Journal of Water Resource and Protection, 5, 2013, pp. 867-875
6. WHO, Guidelines for Drinking-Water Quality, 4th Edition, 2011, pp. 323-324.
7. B.J. Marifias, "Reverse Osmosis Technology for Wastewater Reuse", Water Sci. Technol., 24 (9) , 1991, pp. 215.
8. M.H. Al-Malack, N.S. Abuzaid, A.H. El-Mubarak, "Coagulation of polymeric wastewater discharged by a chemical factory", Water Res. 33, 1999, pp. 521–529.
9. M.I. AGUILAR, J. SAEZ, M. LLORENS, A. SOLER, J.F. ORTUNO, "NUTRIENT REMOVAL AND SLUDGE PRODUCTION IN THE COAGULATION-FLOCCULATION PROCESS", WATER RES. 36, 2002, PP. 2910–2919.
10. P.K. Holt, G.W. Barton, M. Wark, C.A.A. Mitchell, "Quantative comparision between chemical dosaging and electrocoagulation", Colloids Surf. A 211, 2002, pp. 233–248.
11. G. C. Cushnie, Electroplating Wastewater Pollution Technology, Noyes Publications, NJ, 1985.
12. M. A. Zazouli and M. Taghavi, "Phenol Removal from Aqueous Solutions by Electrocoagulation Technology Using Iron Electrodes: Effect of Some Variables", Journal of water Resource and Protection, Vol. 4, 2012, pp. 980-983.
13. A. E. Yilmaz, R. Boncukcuoglu, M. Muhtar Kocakerim and B. Keskinler, "The Investigation of Parameters Affecting boron Removal by Electrocoagulation Method", J. Hazard. Mater., Vol. B125, No. 1-3, 2005, pp. 160-165.
14. F. J. López, E. Jiménez and F. Hernández, "Analytical Study on the Determination of Boron in Environmental Water Samples," Fresenius' , J. Anal. Chem., Vol. 346, No. 10-11, 1993, pp. 984-984.
15. M. M. de la Fuente and E. Mùnoz, "Boron Removal from Industrial Wastewaters by Ion Exchange: An Analytical Control Parameter," Desalination, Vol. 181, No. 1-3, 2005, pp. 207-216
16. X. Chen, G. chen, P. L. Yue, "Electrocagulation and electroflotation of restaurant wastewater", J. Enviro.Eng-ASCE, 126(9), 2000, pp. 858-863.
17. T. Öztürka, , S. Velib, and A. Dimoglo, "The Effect of Seawater Conductivity on the Treatment of Leachate by Electrocoagulation", Chem. Biochem. Eng. Q., 27 (3), 2013, pp. 347–354.

18. H. Liu, X. Zhao and J. Qu, Electrocoagulation in Water Treatment, Electrochemistry for the Environment, Springer Science + Business Media, LLC., 2010.
19. G. Sayiner, F. Kandemirli, A. Dimoglo, "Evaluation of boron removal by electrocoagulation using iron and aluminium electrodes", Desalination, 230, 2008, pp. 205-212.
20. A.J. Bard, R. Parsons, J. Jordan, Standard Potentials in Aqueous Solution, Marcel Dekker, New York, 1985.
21. W.N. Juang, , J.L. Kun, , "Characteristic of boron adsorption on strong-base anion Exchange resin", Ann. Nucl. Energy, 20(7): 1993, pp. 455-462.
22. A. Erdem Yilmaz, R. Boncukcuoglu, M. Muhtar Kocakerim, "An empirical model for parameters affecting energy consumption in boron removal from boron-containing wastewaters by electrocoagulation", J. Hazard. Mater.144, 2005, pp. 101-107.