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Journal of Hazardous Materials 153 (2008) 146–151
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Boron removal from geothermal waters by electrocoagulation

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Received 3 April 2007; received in revised form 12 August 2007; accepted 13 August 2007
Available online 19 August 2007

Abstract

Most of the geothermal waters in Turkey contain extremely high concentration of boron when they are used for irrigation. The use of geothermal waters for irrigation can results in excess amount deposition of boron in soil. On the other hand, a minimal boron concentration is required for irrigational waters. In this study, electrocoagulation (EC) was selected as a treatment process for the removal of boron from thermal waters obtained from Ilıca-Erzurum in Turkey. Current density (CD), pH of solution and temperature of solution were selected as operational parameters. The results showed that boron removal efficiency increased from pH 4.0 to 8.0 and decreased at pH 10.0. Although boron removal efficiency was highest at pH 8.0, energy consumption was very high at this pH value compared to other pH intervals. Boron removal efficiency reached to 95% with increasing current density from 1.5 to 6.0 mA/cm^2, but energy consumption was also increased in this interval. At higher temperatures of solution, such as 313 and 333 K, boron removal efficiency increased. At optimum conditions, boron removal efficiency in geothermal water reached up to 95%.

Keywords: Boron; Electrocoagulation; Geothermal water; Aluminum electrode

1. Introduction

The source of boron being available in nature, mostly as sodium and/or calcium borate, is often linked to the volcanic activities via the agency of hydrothermally generated boron-rich springs that are mixed with the playa waters and precipitate borates. Boron species of many geothermal fields and boron-rich thermal springs present in Turkey are undissociated boric acid (H_3BO_3) and borate ions [$B(OH)_4^-$]. H_3BO_3 is the dominant at low pH values and [$B(OH)_4^-$] is dominant at high pHs (>8–9) [1]. It has been found that boron concentrations change from 1 to 63 mg/L in CO_2-rich thermal waters in the studied fields [1].

Boron contents of thermal waters generally discharged to agricultural areas for irrigation after being used in the thermal baths are accumulated in the soils irrigated and change the biological, chemical and physical properties of the soils. Also, these waters mix with underground waters by passing through the soil and boron compounds constitute complexes with some heavy metal ions, such as Pb, Cu, Ni, Cd, etc. and these complexes are more toxic than those of heavy metals forming them. Consequently, the thermal waters cause some environmental problems in discharge areas and their boron contents should be removed by an appropriate method.

The WHO has given a preliminary limit of 0.3 mg/L for drinking water. The EU regulations are suggesting a guideline of 1.0 mg/L. Most of surface and ground waters are below this limit; however, boron contamination of waters is a concern around the world.

Boron is an essential element for plants only within narrow concentration limits and for this reason, a minimum concentration of boron in irrigation water is needed for some metabolic activities. Boron deficiency in plants may result in reduced growth, yield loss and even death, depending on the severity of deficiency. When boron deficiency is present, stem and root apical meristems often die. Root tips often become swollen and discolored. Leaves show various symptoms, which include drying, thickening, distorting, wilting and chlorotic and necrotic

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doi:10.1016/j.jhazmat.2007.08.030

Table 1
The tolerance of different crops in response to boron in irrigation water

Sensitive 1 mg/L in irrigation water	Semi-sensitive 2 mg/L in irrigation water	Resistant 4 mg/L in irrigation water
Walnut	Sunflower	Asparagus
Plum	Potato	Palm
Pear	Cotton	Date-palm
Apple	Tomato	Sugar beet
Grape	Pea	Clover
Fig	Olive	Broad bean
Cherry	Barley	Bean
Peach	Wheat	Onion
Apricot	Corn	Turnip
Orange	Gruel	Cabbage
Grapefruit	Cruet	Lettuce
Lemon		Carrot

spotting [2]. If boron concentration in irrigation water is only slightly higher than minimum, this will give a negative effect on plant growth and will present signs of boron toxicity. Boron toxicity can affect nearly all crops, but there is a wide range of tolerance among crops. The tolerance of different crops in response to boron in irrigation water was demonstrated in Table 1. 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. In result, although boron is vital as a micronutrient element for plants' growth, it can be detrimental at higher concentrations [3]. In consequence of these reasons, boron levels in drinking and irrigation waters are required to be under control.

Electrochemical technology contributes in many ways to a cleaner environment and covers a very broad range of technology [4]. During the last two decades, a special research field, environmental electrochemistry has been developed. Environmental electrochemistry [5–11] involves electrochemical techniques or methods to remove impurities from gases, liquids and soil to prevent or minimize environmental pollution. Electrocoagulation is an efficient method used for treating various process effluents containing, textile dyes [12,13], nitrate [14], fluoride [15,16], restaurant wastewater [17], arsenic [18], phenolic compounds [19], natural organic matters [20], phosphate [21,22], boron [23], etc.

Electrocoagulation involves the generation of coagulants in situ by dissolving electrically either aluminum or iron ions from, respectively, aluminum or iron electrodes which can be in plate form or packed form of scraps such as steel turnings, millings, etc. 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.

The aim of this paper is to investigate parameters affecting energy consumption in the removal of boron from thermal waters by electrocoagulation, which is a new process, applied to boron-containing thermal water. The process was examined under different values of current density, pH and temperature of solution, in order to determine optimum operating conditions. The electrode material used in this study is aluminum.

2. Experimental

2.1. Materials

Geothermal water samples used in this study were provided from Ilıca-Erzurum, Turkey. The chemical analysis of geothermal water was given in Table 2. The samples filtered with blue band filter paper at room temperature were used for the electrocoagulation experiments.

2.2. Analytical methods

The pH and conductivity were measured by a multimeter (WTW, Multiline), which was freshly calibrated by 2 points (4.01, 7.00) before each test. The analytical determination of boron was done potentiometrically by means of mannitol, which forms a complex compound with boric acid. For this purpose, boron analyses were carried out as 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. A 1 mL 0.5N KOH is equal to 17.41 mg B_2O_3 [24]. This method was selected in order to prevent aluminum interference in boron determination done by spectrophotometric methods such as carmine, azomethine-H and curcumin methods [25].

The removal efficiency of boron in thermal water treated by electrocoagulation is calculated as follows:

$$\eta\,(\%) = \left(\frac{(C_0 - C_e)}{C_0}\right) \times 100 \tag{1}$$

where, η is removal efficiency, C_0, boron concentration at initial and C_e is the boron concentration at equilibrium.

2.3. Electrocoagulation test

A laboratory-scale reactor (16 cm × 10 cm × 10 cm), made of plexiglass, was used in all experiments. Two groups of alternating electrodes being cathodes and anodes (by five plates of each type) made of aluminum with total area of approximately 1000 cm^2 were arranged vertically. The net spacing between the aluminum electrodes was 0.5 cm. Electrodes were connected to a digital DC power supply characterized by the ranges 1.5–6.0 mA/cm^2 for current and 0–30 V for voltage in

Table 2
Chemical and physical analyses of Ilıca geothermal water

Component	mg/L	Component	mg/L
Al^{3+}	0.20	Cl^-	1990.00
Na^+	1731.30	F^-	0.80
K^+	226.50	SO_4^{2-}	2.50
Mg^{2+}	37.80	NO_3^-	9.60
Ca^{2+}	61.60	Hydrophosphate	0.95
Fe^{2+}	1.20	HCO_3^-	1876.00
Mn^{2+}	1.00	Free CO_2	1085.00
NH_4^+	1.65	Boron	24
Temperature (K)	325	pH	6.50

monopolar mode. Two digital multimeters as ampermeter and voltmeter were used to measure the current passing through the circuit and the applied potential, respectively.

The parameters chosen for the experiments were pH, current density and temperature of solution. During the experiments, the electrocoagulation unit was stirred at 150 rpm by a magnetic stirrer and temperature, conductivity and pH of the thermal water were measured by a multimeter. The reactor was fed with 1500 mL of boron containing thermal water at the beginning of each run performed at constant temperature (293 K) except the experiments which effect of temperature of solution on boron removal was investigated. After each run was timed starting with switching the DC power supply on, the residual boron in the samples filtered and taken from the reactor was measured. Electrocoagulation process was schematically demonstrated at authors' previous work [23].

3. Results and discussion

3.1. The effects of parameters

In the runs, it has been investigated the effects of parameters such as pH, current density and temperature on boron removal under the conditions which the reaction time hold in constant.

3.1.1. The effect of pH

The initial pH is one of the important factors in affecting the performance of electrochemical process. It has been established that the pH has a considerable influence on the performance of electrocoagulation process. To investigate this effect, a series of experiments performed using thermal water containing boron of 24 mg/L were carried out at 4.0, 6.0, 8.0 and 10.0 pHs under conditions in which current density of 1.5 mA/cm^2 and stirring speed of 150 rpm were kept constant during experiments. Boron removal efficiency increased with the pH up to 8.0, and then decreased. 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 $Al(OH)_4^-$ in dissolving form at pH 9.0 and does not appear flocks [26]. Because high pH will lead to the formation of $Al(OH)_4^-$, which is soluble and useless for boron removal, experiments were carried at pH 4–10 interval. Maximum 2–3 mL concentrated HNO_3 (w/w, 63%) was added to the solution for constant pH during the experiment period in which pH was rose. Under these conditions, nitrate ion was not expected to be effective on boron removal. According to obtained data in Fig. 1, optimum boron removal reached at pH 8.0 is probably resulting from borate form and Al(III) species which is formed in solution at this pH. On the other hand, the relationship between the energy consumption, pH and conductivity is shown in Fig. 2. It was seen in Fig. 3 that the lowest energy consumption curve was obtained in the experiments carried out with pH 10.0 because the solution had the highest conductivity of 9.31 mS/cm, while specific conductivity of solution with pH 8.0 remained at 7.7 mS/cm. As expected, lower energy consumption was obtained at higher solution conductivity. The effect of conductivity on electrical energy consumption

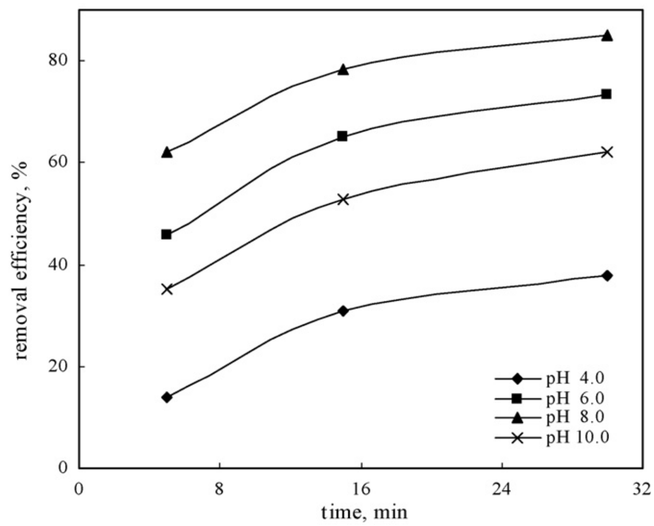

Fig. 1. The effect of pH on boron removal (1.5 mA/cm^2 current density, 293 K solution temperature and 150 rpm stirring speed).

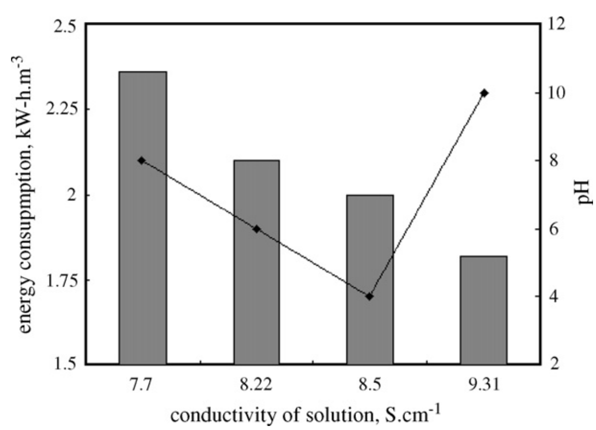

Fig. 2. The relationship between energy consumption, pH and solution conductivity.

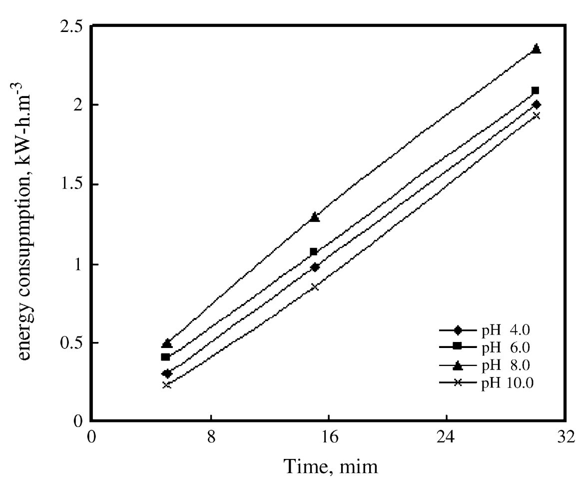

Fig. 3. The effect of pH on energy consumption (1.5 mA/cm^2 current density, 293 K solution temperature and 150 rpm stirring speed).

can be explained with the following equations;

$$W = \frac{V\,I\,t}{\nu} \quad (2)$$

where, W, electrical energy consumption (Wh/m^3), V, potential (volt), I, current (ampere), t, time (h) and ν, volume of the solution (m^3). Applied potential could be explained with the following equation;

$$V = I\,r \quad (3)$$

where, r, resistance (ohm). From Eqs. (2) and (3), following equation could be obtained;

$$W = \frac{I^2\,r\,t}{\nu} \quad (4)$$

Electrical conduction is an electrical phenomenon in which a material (solid or otherwise) contains movable particles with electric charge, which can carry electricity. When a difference of electrical potential is applied to a conductor, an electric current appears. Conductivity stated as the inverse of electrical resistivity, is defined as the ratio of the current density to the electric field strength and has the SI units of Siemens per meter (S/m). Increasing electrical conductivity caused to decrease energy consumption due to relationship between electrical conductivity and resistance. The lower and higher pH of solution than pH 8.0 caused the rise of electrical conductivity. Thus, high conductivity values of solution caused low resistance values and low energy consumption.

3.1.2. The effect of current density

It is well known that current not only determines the coagulant dosage rate but also the bubble production rate, size and the flocks growth, which can influence the treatment efficiency of the electrocoagulation. Thus, this parameter should have a significant impact on removal efficiencies of pollutants. To investigate the effect of current density on the energy consumption, a series of experiments were carried out under the experimental conditions of current density being varied from 1.5 to 6.0 mA/cm^2, solution pH of 8.0, temperature of 20 °C and stirring speed of 150 rpm. The highest current (6.0 mA/cm^2) produced the quickest removal rate, with a 92.2% concentration reduction occurring just after 30 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 [27]. Indeed, the amounts of aluminum and hydroxide ions generated within the electrocoagulation cell at a given time are related to the current flow, using Faraday's law:

$$m = \frac{(I\,t\,M)}{(z\,F)} \quad (5)$$

where I is the current intensity, t is the time, M is the molecular weight of aluminum or hydroxide ion (g/mol), z is the number of electrons transferred in the reaction (3 for aluminum and 1 for hydroxide) and F is the Faraday's constant (96,486 C/mol). The results obtained are shown graphically in Fig. 4. Although that current density was increased from 1.5 to 6.0 mA/cm^2 increased

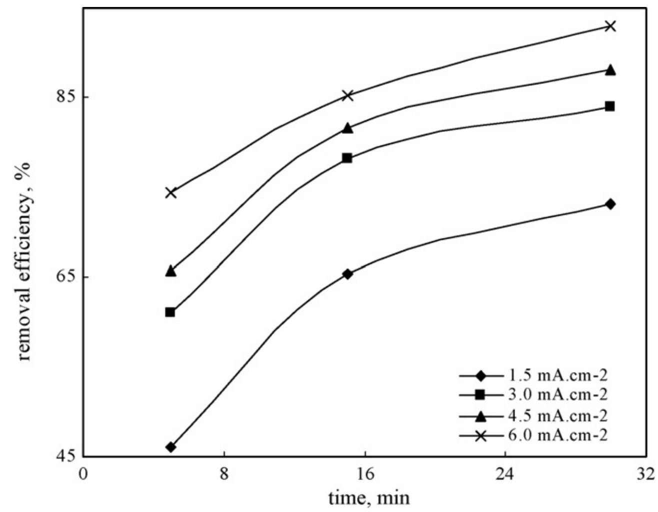

Fig. 4. The effect of current density on boron removal (pH 8.0, 293 K solution temperature and 150 rpm stirring speed).

from 73.1 to 93% of boron removal efficiency, energy consumption reached from 0.73 to 12.8 kWh/m^3. The obtained results for energy consumption were demonstrated in Fig. 5. The relationship between current density, boron removal efficiency and energy consumption was demonstrated in Fig. 6. High electrical energy consumption with increasing current density was an expected result because energy consumption impressed linearly current density as seen in Eq. (2). Although higher current density caused to solve more electrode material and remove more pollutant, this state was not desired in view of electrical energy consumption.

3.1.3. The effect of solution temperature

The effect of temperature on the boron removal was examined with 293, 313 and 333 K. Experiments during which current density of 3.0 mA/cm^2, stirring speed of 150 rpm and optimum pH of 8.0 were kept constant showed that increasing

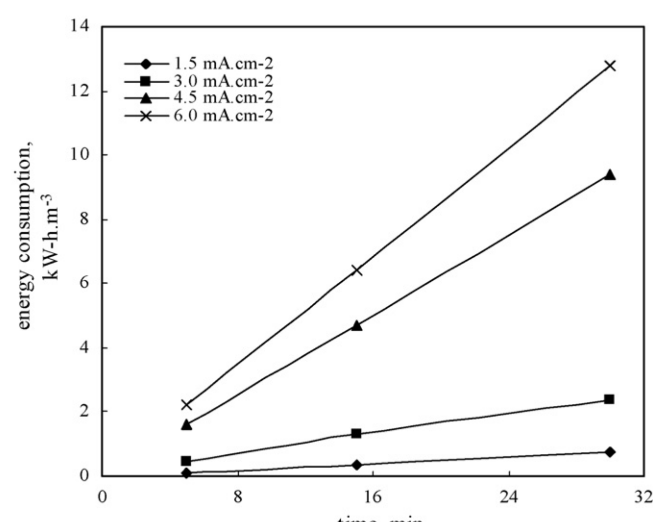

Fig. 5. The effect of current density on energy consumption (pH 8.0, 293 K solution temperature and 150 rpm stirring speed).

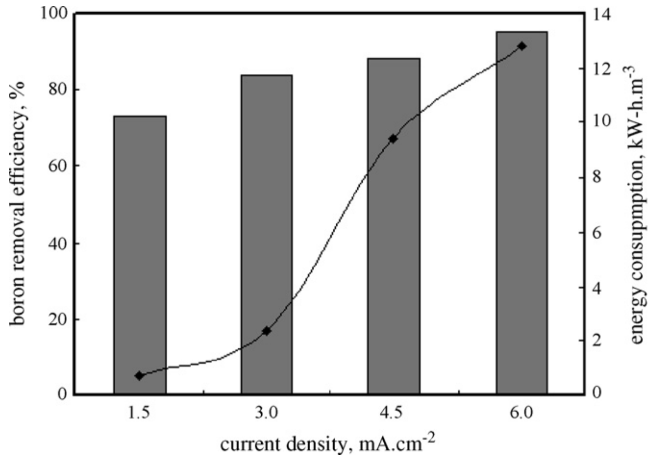

Fig. 6. The relationship between current density, boron removal efficiency and energy consumption (293 K solution temperature, pH 8.0 and 150 rpm stirring speed).

temperature of solution increased boron removal efficiency. The electrochemical reaction rate, like most other chemical reaction rates, increases when the temperature of the solution increases. As shown in Fig. 7, when the temperature was varied from 293 to 333 K, the boron removal efficiency increased from 84 to 96% after 30 min reaction period. Formed $Al(OH)_3$ flocks reacted faster and more to constant pollutant because the reason could be due to increase in mobility and collisions of ions with hydroxide polymer. As a result, boron removal efficiency increased with increasing temperature. When Table 2 was examined, it was seen that thermal water consists of a lot of different anions and cations. As a result of increasing solution temperature, it was expected that these ions reacted to flocks and formed gel on anode surface. Applied potential increased due to gel on anode surface. Consequently, increasing applied potential caused increasing energy consumption. The results were shown graphically in Figs. 7 and 8, respectively.

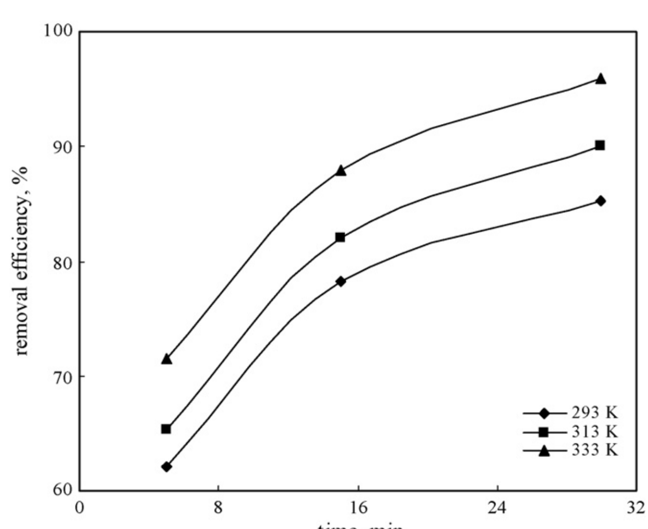

Fig. 7. The effect of temperature on boron removal (3.0 mA/m^2 current density, pH 8.0 and 150 rpm stirring speed).

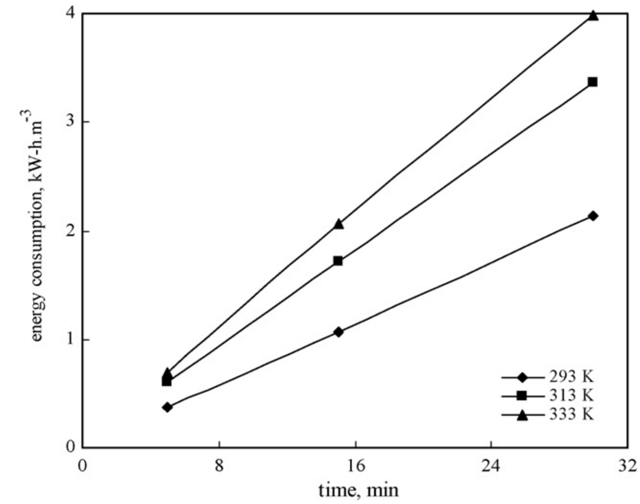

Fig. 8. The effect of temperature on energy consumption (3.0 mA/m^2 current density, pH 8.0 and 150 rpm stirring speed).

4. Conclusions

Based on the results of experiments, the following conclusions may be obtained:

(1) After the treatment, EC method provided clear, colorless and odorless water.
(2) The removal rate of the boron in thermal waters by EC was affected by the CD, pH value of the solution and its temperature. This rate was very fast with mentioned method.
(3) In this work, it was shown that the EC treatment achieves an effective boron removal from thermal waters. For 1500 mL thermal water containing boron as much as 24 mg/L, boron removal efficiency was 96%, for the pH value of 8.0, electrolysis time of 30 min and CD of 6.0 mA/cm^2.
(4) Boron removal is more effective at higher temperatures compared to lower temperatures. Because of a high temperature of approximately 325 K, this better boron removal condition is naturally satisfied for thermal waters. The thermal water was not required to warm up because this water has a high temperature of approximately 325 K.
(5) After EC process, mentioned above, boron concentration decreased to less than 1 mg/L, so that effluent water could be used for irrigation.

Acknowledgement

Authors are grateful to The Scientific and Technological Research Council of Turkey, for providing financial support with grant no. ÇAYDAG/105Y036.

References

[1] S. Barth, Utilization of boron as a critical parameter in water quality for thermal and mineral water resources in SW German and N Switzerland, Environ. Geol. 40 (1–2) (2000).
[2] Ü. Gemici, G. Tarcan, Distribution of boron in thermal waters of western Anatolia, Turkey, and examples of their environmental impacts, Environ. Geol. (2002) 1–8.

[3] EPA, Toxicological review report of boron and its compounds, CA No. 7440-42-8, 2001.
[4] G.C. Cushnie, Electroplating Wastewater Pollution Technology, Noyes Publications, NJ, USA, 1985.
[5] G. Kreysa, K. Jüttner, F. Lapique, A. Storck, A.A. Wragg, Electrochemical Engineering and Energy, Plenum Press, New York, 1994.
[6] K. Rajeshwar, J.G. Ibanez, Environmental Electrochemistry: Fundamentals and Applications in Pollution Abatement, Academic Press, London, 1997.
[7] J.D. Genders, N.L. Weinberg, Electrochemistry for a Cleaner Environment, The Electrochemistry Company, Inc., New York, 1992.
[8] D. Pletcher, F.C. Walsh, Industrial Electrochemistry, second ed., Blackie, London, 1993.
[9] K. Rajeshwar, J.G. Ibanez, G.M. Swain, Electrochemistry and the environment, J. Appl. Electrochem. 24 (1994) 1077.
[10] C.A.C. Sequeira, Environmentally Oriented Electrochemistry, Elsevier, Amsterdam, 1994.
[11] K. Jüttner, U. Galla, H. Schmieder, Electrochemical approaches to environmental problems in the process industry, Electrochim. Acta 45 (2000) 3575.
[12] O.T. Can, M. Bayramoglu, M. Kobya, Decolorization of reactive dye solutions by electrocoagulation using aluminum electrodes, Ind. Eng. Chem. Res. 42 (2003) 3391–3396.
[13] H. Daneshvar, A. Ashassi-Sorkhabi, Decolorization of orange II by electrocoagulation method, Sep. Purif. Technol. 31 (2003) 153–162.
[14] A.S. Koparal, U.B. Ogutveren, Removal of nitrate from water by electroreduction and electrocoagulation, J. Hazard. Mater. B89 (2002) 83–94.
[15] F. Shen, X. Chen, P. Gao, G. Chen, Electrochemical removal of fluoride ions from industrial wastewater, Chem. Eng. Sci. 58 (2003) 987–993.
[16] C.Y. Hu, S.L. Lo, W.H. Kuan, Y.D. Lee, Removal of fluoride from semiconductor wastewater by electrocoagulation–flotation, Water Res. 39 (2005) 895–901.
[17] X. Chen, G. Chen, P.L. Yue, Separation of pollutants from restaurant wastewater by electrocoagulation, Sep. Purif. Technol. 19 (2000) 65–76.
[18] P.R. Kumar, S. Chaudhari, K.C. Khilar, S.P. Mahajan, Removal of arsenic from water by electrocoagulation, Chemosphere 55 (2004) 1245–1252.
[19] N. Adhoum, L. Monser, Decolourization and removal of phenolic compounds from olive mill wastewater by electrocoagulation, Chem. Eng. Prog. 43 (2004) 1281–1287.
[20] Y.Ş. Yildiz, A.S. Koparal, S. İrdemez, B. Keskinler, Electrocoagulation of synthetically prepared waters containing high concentration of NOM using iron cast electrodes, J. Hazard. Mater. B139 (2007) 373–380.
[21] Ş. İrdemez, Y.Ş. Yildiz, V. Tosunoğlu, Optimization of phosphate removal from wastewater by electrocoagulation with aluminum plate electrodes, Sep. Purif. Technol. 52 (2006) 394–401.
[22] Ş. İrdemez, N. Demircioğlu, Y.Ş. Yildiz, The effects of pH on phosphate removal from wastewater by electrocoagulation with iron plate electrodes, J. Hazard. Mater. B137 (2006) 1231–1235.
[23] A.E. Yılmaz, R. Boncukcuoglu, M.M. Kocakerim, B. Keskinler, The investigation of parameters affecting boron removal by electrocoagulation method, J. Hazard. Mater. B125 (2005) 160–165.
[24] A.A. Nemodurk, Z.K. Karalova, Analytical chemistry of boron, Israel-Program for Scientific Translations, Jerusalem, 1965.
[25] R.N. Sah, P.H. Brown, Boron determination—a review of analytical methods, Microchem. J. 56 (1997) 285–304.
[26] A.J. Bard, R. Parsons, J. Jordan, Standard Potentials in Aqueous Solution, Marcel Dekker, New York, 1985.
[27] P.H. Holt, G.W. Barton, M. Wark, A.A. Mitchell, A quantitative comparison between chemical dosing and electrocoagulation, Colloids Surf. A Physicochem. Eng. Aspects 211 (2002) 233–248.