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Arsenic and boron removal from spring and groundwater samples in boron mining regions of Turkey by electrocoagulation and ion-exchange consecutive processes

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ABSTRACT

Boron (B) and arsenic (As) are two important contaminants detected in the spring and groundwater around the Bigadiç borate mines in Turkey which have the largest colemanite and ulexite deposits in the world. In this study, electrocoagulation (EC) process was used for the removal of arsenic from waters since EC was capable of removing arsenic to trace levels. The removal efficiencies of arsenic from spring and groundwater samples containing different arsenic concentrations of 36–1021 µg/L at 0.025–0.10 A and operating time of 0–60 min were achieved >97–99.9% at 2–16 min for Fe plate electrodes to meet the permissible level of arsenic effluent concentration of <10 µg/L. Energy and electrode consumptions for arsenic removal efficiency were 0.00429 kWh/m^3 and 0.00372 kg/m^3 for 0.025 A, 0.00529 kWh/m^3 and 0.00496 kg/m^3 for 0.05 A, and 0.00917 kWh/m^3 and 0.00992 kg/m^3 for 0.10 A. However, the EC was unsuccessful for the removal of B. B removal efficiencies at 0.025, 0.05, and 0.10 A were determined as 3.4, 3.9, and 4.6%, respectively. Effluent pH values were noticed to increase from 8 to 10 during the EC process and this was an advantage to remove B from the sample using ion-exchange process at pH 8–11. For that reason, Amberlite IRA-743 ion-exchange resin was selected to treat B in the effluents and effect of resin dosage (0.025–3 g) on the B removal efficiency was performed. A removal efficiency of 99–100% for B in the spring and groundwater samples was obtained. As the resin dosages were increased from 0.025 to 3 g, adsorption capacity was observed to decrease from 60 to 7.4 mg B/g resin. As effluent concentration of 1 mg/L was considered, amount of resin dosage for B removal was 0.75 g to reduce B concentration from 90.11 to 0.56 mg/L. The EC and ion exchange processes together were very successful for the removals of arsenic and boron from natural waters in the boron mining regions.

Keywords: Arsenic contamination; Spring and groundwater; Electrocoagulation; Boron removal

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1. Introduction

Turkey has the largest borate reserves in the world. The borate deposits of Turkey occur in western Anatolia within an area stretching roughly 300 km east-west and 150 km north-south. Approximately 80% of the total world borate reserves lies in the region [1]. The known borate reserves in Turkey are located in four main districts: Balıkesir-Bigadiç, Kütahya-Emet-Hisarcık, Eskişehir-Kırka, and Bursa-Kestelek [2]. Turkish production is controlled by the Eti Mine Cooperation, the national mining enterprise supplying most of the commercially traded tincal, ulexite, colemanite and borax from the borate mines [3,4]. However, arsenic and boron contaminations in groundwater and around borate deposits were caused by naturally occurring arsenic dissolution from a borate bearing clay zone due to the leaching of arsenic bearing minerals such as realgar and orpiment [5,6]. In addition, numerous cases of As and B pollutions in natural water sources around mining deposit, geothermal and coalfields in Western Anatolia of Turkey were reported in recent years. As and B concentrations in surface and groundwaters are 0.5–562 µg As/L and 0.21–3.6 mg B/L for

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Kütahya-Simav [7], 0.7–170.1 µg As/L and 0.1–9.5 mg B/L for İzmir-Balçova Plains in geothermal fields [8], 10–10700 µg As/L and 300–500 µg As/L for Iğdeköy and Dulkadir villages of the Kütahya [9,10], and 70–7754 µg As/L and 0.2–4.4 mg B/L for Kütahya-Emet-Hisarcik [11].

Amount of arsenic in colemanite and ulexite minerals in these deposits was around 70 mg/kg, coinciding with the high As concentrations in groundwater in the borate mine region. The concentrations of As and B in these waters range from 33 to 911 µg As/L and from 0.05 to 640 mg B/L, respectively, and the greatest B concentration of 260 mg/L was detected at the open pit mines [1,12,13]. Arsenic is one of the most important drinking water pollutants because of its carcinogenicity and toxicity. Concentrations of As and B in spring water and groundwater for drinking and irrigation are greater than the safe levels. 30.9% and 5.35% of individuals were reported for arsenic-related skin disorders including keratosis, Bowen's disease, basal-cell-carcinoma, and squamous-cell carcinomain Iğdeköy and Dulkadir villages because of consumption of arsenic contaminated drinking waters [16]. Boron (B) has a positive effect on functioning of many organs but long-term consumption of water and food with increased boron content results in creation of problems with cardiovascular, coronary, nervous and reproductive systems. Excess of boron can be particularly dangerous for pregnant women as it increases the risk of birth pathology. High daily doses of boron cause testicular atrophy and degeneration [17]. In addition, boron concentrations >1 mg/L in irrigation water can cause plant damage. Therefore, drinking water standards for As and B suggested by the World Health Organization (WHO) are set as 10 µg/L and 2.4 mg/L, respectively [17,18].

Indeed, As and B from waters are the most difficult components to remove using one water treatment method as compared to removal of other contaminants in waters. Arsenic can be removed from surface and groundwater supplies by coagulation/filtration process using ferric and aluminium based salts [19,20]. The effective pH for arsenic removal was reported to be 5–7 with aluminium ions, and 5–8 for ferric ions [21]. Moreover, various technologies are available for the removal of arsenic from contaminated water including adsorption [22,23–30], Fe-Mn oxidation and enhanced softening [31], ion-exchange [32,33], and membrane processes [34,35]. In recent years, electrocoagulation (EC) process using iron and aluminium anodes has been shown to be a promising and alternative method for arsenic removal [36–39]. EC process unlike other processes has advantages such as higher removal efficiency (>99%), no pH adjustment, no chemical requirement for pre-oxidation of As(III) to As(V), simplicity to operate, no secondary pollutants such as chloride and sulphate, compact treatment facility, and relatively cost-effective [38]. On the other hand, commonly used methods for boron removal from water are membrane processes, reverse osmosis and nanofiltration [40–42], adsorption [43], electrodialysis [44,45], and ion-exchange [46], The removal efficiency with reverse osmosis (RO) was achieved about 40–80% and over 90% in alkaline solutions at a pH of 10–11 [47]. But RO process was not effective because of the membrane cost, scaling and stability. Boron removal by electrodialysis from wastewaters was obtained as 40–85% [48,49]. Another method for removal of boron is chemical coagulation through dilute boron solutions (1.6–0.16 mg/L) and could be treated up to 90% using aluminium sulphate and calcium hydroxide. In addition, boron removal by alum coagulation from industrial effluents was obtained as 75% [50]. Boron removals from aqueous solutions and geothermal waters were determined to be within the range of 70–95% by the EC process using aluminium anodes [51,52]. The methods like chemical coagulation and electrocoagulation would produce problems such as voluminous amount of alum sludge for disposal and residual aluminium toxicity in the treated water. Adsorption and ion-exchanges for boron removal from water seems to be the most effective treatment methods [53]. The technology commonly used for the removal of boron from aqueous solutions is ion-exchange process and commercial chelating resins as Amberlite IRA-743, Purolite S-108, and Diaion CRB 05 were useful for removal of boron in the range of 93 and 98% [54–56]. Boron removal efficiency and breakthrough capacity from the drainage waters (16–390 mg B/L) of Bigadiç boron mines by Amberlite IRA743 was 90% and 2.25–3.40 mg B/mL resin [57].

In this study, arsenic and boron removals in spring and groundwater from open-pit boron mines around Bigadiç were investigated with electrocoagulation using iron electrodes and ion-exchange processes. Firstly, removal of arsenic and boron from natural water samples in a batch EC reactor was achieved with iron (Fe) plate anodes. Effects of operating time and applied current on the removal efficiency were studied to determine the optimum operating parameters. Secondly, effluents from the EC process were treated for removal of boron with a commercial resin (Amberlite IRA-743) and effect of resin dosage on the B removal efficiency was investigated.

2. Material and methods

2.1. Material and methods

2.1.1. Characterization of natural water samples

Bigadiç deposits formed within Neogene perennial saline lake sediments [1]. The Turkish Borax Company has been operating mines in the Bigadiç borate deposit areas since 1976 and borate minerals are dominantly colemanite and ulexite. There are three main borate mines: namely Simav, Tülü and Acep borate open pits in the Bigadiç region and these open pits are 10 km from downtown Bigadiç. Groundwater in borate deposit areas is located in the fractures of Neogene rocks, alternating terrestrial sediments and volcanic rocks [1,14]. Generally, springs are found along the contact of the alternating beds of permeable and impermeable (clayey levels) units; these springs meet part of the water demand for drinking and agricultural purposes for the people in the villages. People live in villages and towns and around the mine region. The arsenic and boron contaminated waters are mostly observed in spring waters such as SW-1 (spring water): Küçük Spring Fountain, SW-2: Osmanca Village Spring Fountain, SW-3: Ince Memed Spring Fountain and SW-4: Cuma Spring Fountain spring in Iskele town in the Bigadiç district, and samples from spring water in this study were taken as pointed in Fig. 1. Therefore, some of the springs are abandoned and water is supplied by transportation from other water sources. However, some spring waters with relatively high arsenic and

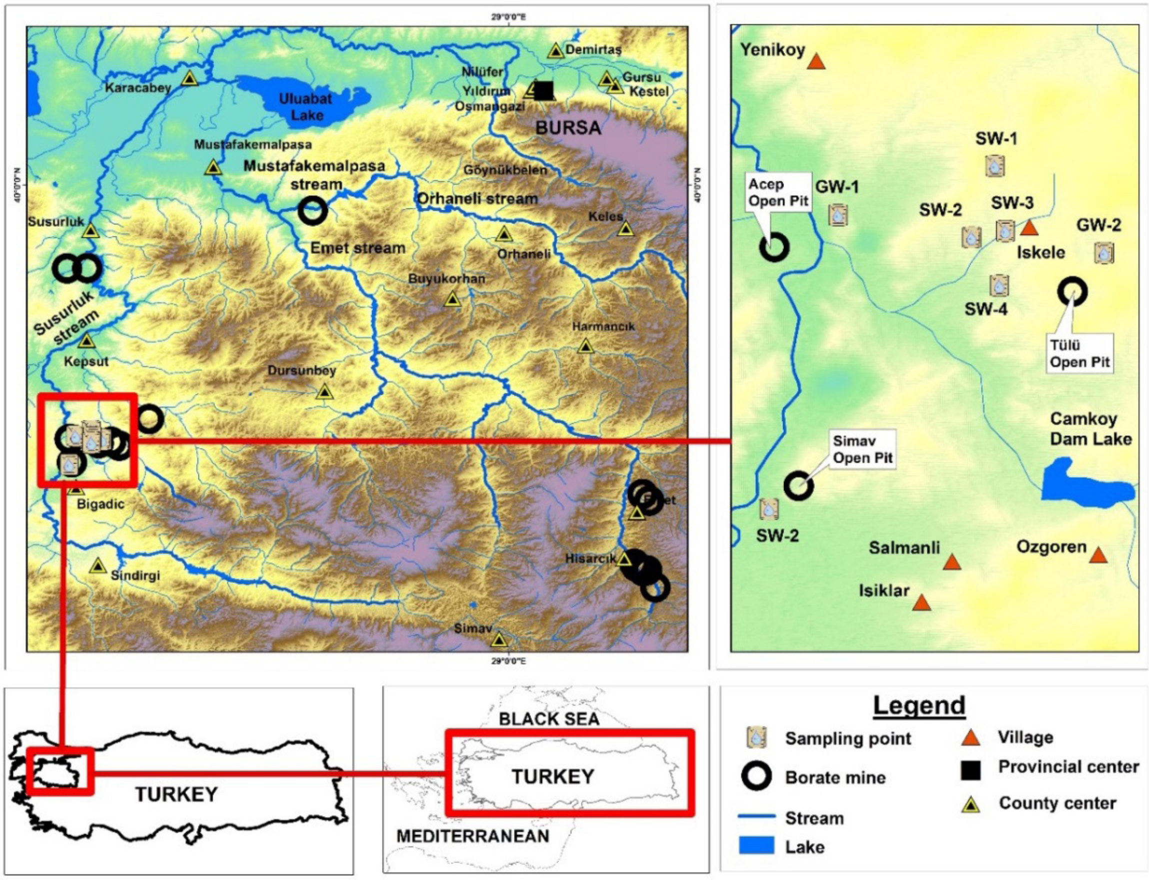

Fig. 1. Map location of borate mine regions in Turkey and locations of water sample sites around Bigadiç borate area.

boron contents are still being used by the people living in these villages due to the inadequate supply of water. Moreover, samples were collected from a spring fountain (SW-5) near Simav boron open pit, and groundwater (GW) within Tülü (GW-1) and Acep (GW-2) open pits (Fig. 1). The climate characterized by arid, sunny summers and wet, cold winters in Bigadiç is transitive between the Mediterranean and Black Sea climate regions. Autumn is long and spring is short and rainy. The mean precipitation is around 570 mm. The yearly average temperature is 14.5°C.

Water demands for drinking, agricultural and animal purposes for the people in the settlements around the Bigadiç borate deposits have been supplied mostly by springs, groundwater and surface waters for years. Groundwater from most of the springs is in contact with the borate mineral bearing rocks of the lower and upper borate zones. Parameters such as pH, temperature, electrical conductivity (κ) and total dissolved solids (TDS) were measured in the field with portable devices. After making these measurements, the samples were filtered through 0.45 µm filter papers and preserved for analysis. Each sample was stored in two polyethylene bottles. One of them was acidified with HCl for cation analysis. The other was kept un-acidified for chloride, sulphate and alkalinity analyses. Samples stored at 4°C for no more than 1 week were analysed in the Instrumental Analyses Laboratory of Environmental Engineering Department. The results are represented in Table 1.

2.1.2. Experimental set-ups and procedures

EC studies: The experimental set-up for the EC reactor was reported elsewhere [38]. The EC studies were carried out in a 1.0 L solution capacity in a batch glass reactor with a dimension of 12 cm × 11 cm × 11 cm at a constant temperature of 20°C. The solution was constantly stirred at a rate of 400 rpm by means of a magnetic bar (Heidolp 3600 model) to reduce the mass transport over potential of the EC reactor. Four rectangular plate electrodes, two anodes and two cathodes of the same dimensions (5.0 cm × 7.3 cm × 0.3 cm) with purity of 99.5% were placed in the reactor. Total effective electrode area was 219 cm^2 and the spacing between the electrodes was 1 cm. The electrodes were placed into the reactor at monopolar parallel connection mode. The electrodes were connected to a digital DC power supply (Agilent 6675A model). During each experimental run, 0.85 L of spring or groundwater containing arsenic was placed into the EC reactor. Current was held constant at desired values for each run and the experiment was started. The samples at the different operating times taken from the EC reactor were filtered using a 0.45 µm membrane filter and metal concentrations were determined. At the end of the run, the electrodes were washed thoroughly with water to remove any solid residues on the surfaces, dried and reweighed. The sludge after the EC experiment was dried at 105°C.

Table 1
Chemical analyses of natural water samples

Samples	pH (–)	κ (μS/cm)	TDS (mg/L)	HCO_3^- (mg/L)	B (mg/L)	PO_4-P (mg/L)	SO_4^{2-} (mg/L)	Cl^- (mg/L)	Mg (mg/L)	Ca (mg/L)	Si (mg/L)	As (μg/L)
SW-1	8.67	702	303	356	14.39	1.35	33	10	54.92	61.2	26.53	36.03
SW-2	8.62	904	387	444	6.16	1.16	23	11	70.06	81.2	30.05	113.5
SW-3	8.92	1004	431	440	27.38	1.52	30	9	74.74	79.6	28.64	185.9
SW-4	8.88	680	290	425	9.50	1.54	42	17	67.71	54.2	27.65	706.5
SW-5	8.72	1082	468	598	93.67	1.95	63	19	117.1	90.1	21.21	800.5
GW-1	9.24	1844	799	480	336.6	1.45	130	6.5	43.30	222.8	11.17	1020.5
GW-2	9.29	1084	466	328	226.7	0.99	520	6.3	14.76	188.1	11.59	300.5

SW-1: Küçükpinar spring fountain, *SW-2*: Osmanca Village spring fountain, *SW-3*: Cuma spring fountain, *SW-4*: Ince Memed spring fountain, *SW-5*: Simav spring fountain, *GW-1*: Acep open pit mining groundwater, *GW-2*: Tülü open pit mining groundwater.

Ion-exchange studies: A commercial anion exchange resin, Amberlite IRA-743 supplied from Merck Darmstadt-Germany in this study was used (total capacity: 0.70 eq/L, harmonic mean size: 0.50–0.70 mm, shipping weight: 700 g/L, moisture holding capacity: 48–54%) in the study. Having Macro-porous polystyrene matrix on which N-methylglucamine functional group is attached makes this resin one of the most boron selective adsorbents. Therefore, sample treated by the EC process was subject to filtration to continue boron removal with Amberlite IRA-743 resin. A series of batch ion-exchange tests were conducted to evaluate resin dosage. All the tests were done in capped volumetric flask (100 mL) by adding different resin dosages (0.025–3 g) and 50 mL of spring or groundwater samples. Temperature was kept constant at 25 ± 1°C in a water bath with shaker. Shaking speed was 150 rpm. The adsorbent and solution mixtures were shaken 24 h. After the samples were filtrated, boron in supernatants was analysed. The concentration of boron was analysed using inductively coupled plasma optical emission spectrometer (ICP-OES, PerkinElmer Optima 7000 DV model).

2.1.3. Analytical methods

The chemical analyses of all water samples were carried out according to standard methods [58]. The samples were analysed for As and B after the EC and B after ion-exchange process. Boron and arsenic concentrations in the solutions were measured using an ICP-OES. ICP-OES detection limit was 0.1 μg/L for As and 0.05 mg/L for B. Total arsenic determination requires reducing using KI (10%) and ascorbic acid to convert As(V) to As(III) prior to the arsine formation step. In this study, the water sample (10 mL) was first mixed with 1 mL HCl (10%) and 1 mL of reducing agent (5% KI and 5% ascorbic acid), and then allowed to react for about 60 min at dark place to reduce As(V) to As(III). The concentrations of other cations and elements in the samples were determined by ICP-OES. Anions such as sulphate, chloride and phosphate in natural water samples were determined by an ion chromatography (Shimadzu HIC-20A). Alkalinity was determined by titration following accredited testing procedures. The pH and temperature of water samples were measured using a pH meter (Hach Lange HQ40d model) and the conductivity and TDS were determined with a conductivity meter (Mettler Toledo SG3 model). All the chemical reagents used were of analytical grade. The experiments were repeated twice. The experimental error was below 2% and the average data were reported in this study.

3. Result and discussion

3.1. Arsenic removal with the electrocoagulation process

Arsenic removals in natural water samples obtained from Bigadiç borax open pits and near surroundings were investigated with respect to applied currents and operating EC times since people in town use water for daily needs and drinking purposes. Results of the water samples illustrated in Table 1 are shown in Fig. 2. Total As and B concentrations in Iskele town, Bigadiç where one of spring water is located in Küçükpınar spring fountain (SW-1) were measured as 36.03 μg/L and 14.39 mg/L. The applied current and operating time varied in the range of 0.025–0.10 A and 0–10 min in the EC process. Arsenic removal efficiency was performed with different applied currents in the EC process in order to meet the permissible WHO limit value for the effluent concentration (<10 μg/L). Arsenic removal efficiency needed for SW-1 to meet the permissible WHO limit value was achieved with an operating time of 3 min (C_f of 7.6 μg/L) for 0.025 A, 2 min (C_f of 8.9 μg/L) for 0.05 A, and 2 min (C_f of 5.3 μg/L) for 0.10 A (Fig. 2(a)). Effluent final pH (pH_f) values at 10 min were 8.83 for 0.025 A, 8.91 for 0.05 A and 9.10 for 0.10 A.

B removal efficiencies at 0.025, 0.05, and 0.10 A were determined as 3.4, 3.9, and 4.6%, respectively. Energy and electrode consumptions for arsenic removal efficiency were 0.00429 kWh/m^3 and 0.00372 kg/m^3 for 0.025 A, 0.00529 kWh/m^3 and 0.00496 kg/m^3 for 0.05 A, and 0.00917 kWh/m^3 and 0.00992 kg/m^3 for 0.10 A. Moreover, charge loading ($q = i \times t_{EC}$) increased along with EC time but, minimum time required for the removal of arsenic at 0.025, 0.05 and 0.10 A was 10 min.

As and B concentrations in Osmanca Village spring fountain (SW-2) near Bigadiç-Iskele town were 113.5 μg/L and 6.16 mg/L, respectively. Effluent arsenic concentrations reduced from 113.5 to 8.3 μg/L for 0.025 A and from 113.5 to 4.6 μg/L for 0.05 A at 8 min, and from 113.5 to 6.3 μg/L for 0.10 A at 6 min (Fig. 2b). Final pH values at an oper-

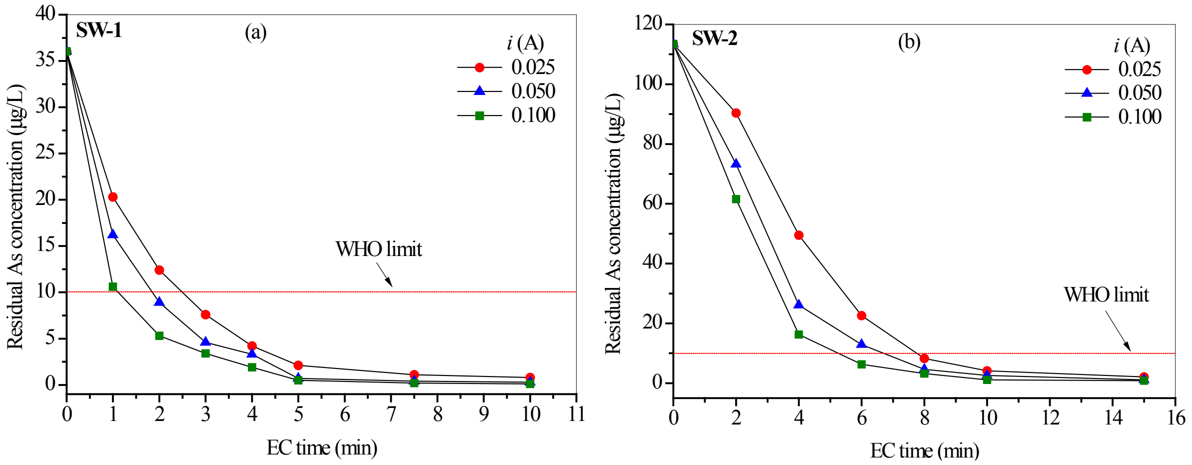

Fig. 2. Arsenic removal efficiencies at different applied currents for SW-1 and SW-2 in the EC process.

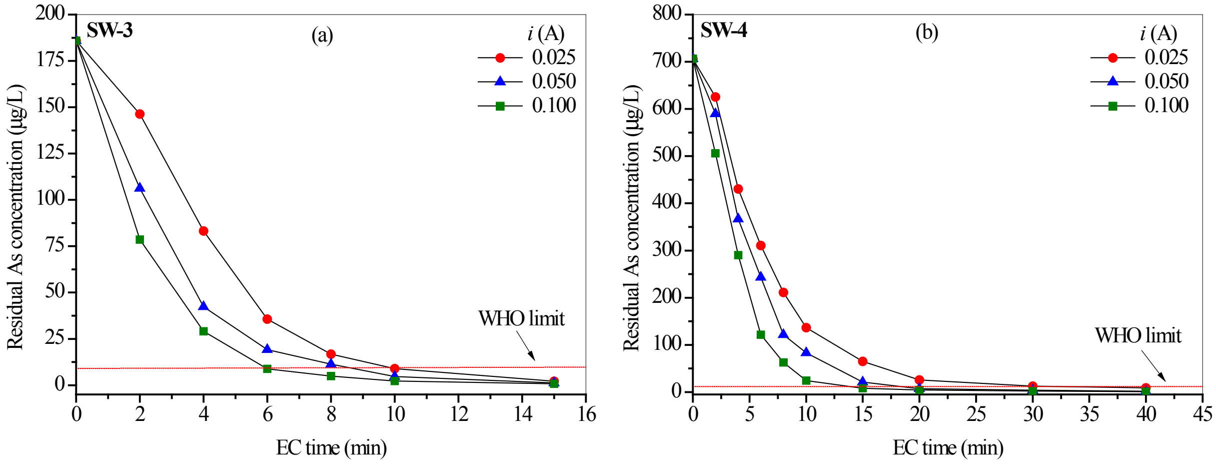

Fig. 3. Arsenic removal efficiencies for SW-3 and SW-4 at different applied currents in the EC process.

ating time of 15 min for 0.025, 0.05 and 0.10 A were 8.71, 8.83 and 8.95, respectively. Charge loading, energy and electrode consumptions at these conditions were 12 C, 0.00733 kWh/m^3 and 0.00992 kg/m^3 for 0.025 A, 24 C, 0.0104 kWh/m^3 and 0.0199 kg/m^3 for 0.05 A and 36 C, 0.0131 kWh/m^3 and 0.0298 kg/m^3. Arsenic removal efficiency for SW-2 increased with the increase in applied currents which led to a decrease in operating time and increase in energy and electrode consumptions. B removal efficiencies at 15 min of EC time were found to be 4.2% for 0.025 A, 4.7% for 0.05 A and 5.8% for 0.10 A.

Arsenic removal efficiencies at 0.025, 0.05 and 0.10 A for Cuma Spring Fountain in Iskele town (initial concentrations of SW-3: 185.9 µg As/L and B of 27.38 mg/L) were 95.21% at 10 min, 97.5% at 10 min, and 95.3% at 6 min, respectively (Fig. 3a). Effluent pH at 15 min were 9.02 for 0.025 A, 9.14 for 0.05 A and 9.21 for 0.10 A. According to the permissible WHO limit value, required charge loading, energy and electrode consumptions were calculated as 15 C, 0.00917 kWh/m^3, 0.0124 kg/m^3 for 0.025 A; 30 C, 0.013 kWh/m^3 and 0.0248 kg/m^3 for 0.05 A; and 36 C, 0.0131 kWh/m^3 and 0.0298 kg/m^3, respectively. Effluent B concentrations for 0.025, 0.05 and 0.10 A at 20 min of EC time were 26.2, 25.9, and 24.8 mg/L, respectively.

High As and B concentrations in SW-4 (Ince Memed Spring Fountain) used by residents in Bigadiç-Iskele town were determined as 706.5 µg/L and 9.5 mg/L, respectively. Effluent arsenic concentrations at 0.025, 0.05 and 0.10 A in the EC process were 8.9 µg/L at 40 min, 7.4 µg/L at 20 min, and 8.3 µg/L at 15 min, respectively (Fig. 3b). Effluent B concentrations for 0.025, 0.05 and 0.10 A at 40 min were 9.1, 8.9 and 8.7 mg/L. pH_f for 0.025, 0.05 and 0.10 A at 40 min were 8.93, 9.1 and 9.12, respectively. The required charge loadings at the optimum EC times were calculated as 60, 60 and 90°C. Energy and electrode consumptions at these conditions were 0.0367 kWh/m^3 and 0.0496 kg/m^3 for 0.025 A; 0.0261 kWh/m^3 and 0.0496 kg/m^3 for 0.05 A; and 0.0327 kWh/m^3 and 0.0744 kg/m^3 for 0.10 A, respectively.

The highest B (93.67 mg/L) and As (800.5 µg/L) concentrations were found in SW-5 (Simav Spring Fountain). Arsenic removal efficiencies for the optimum EC times at 0.025, 0.05 and 0.10 A were 99.1% (C_f of 7.3 µg/L) at 40 min, 98.93% (C_f of 8.6 µg/L) at 20 min, and 99.1% (C_f of 7.4 µg/L) at 15 min, respectively (Fig. 4(a)). pH_f at 40 min for 0.025, 0.05 and 0.10 A were 8.81, 8.94 and 9.10, respectively. At a charge loading of 60°C, energy and electrode consumptions were 0.0367 kWh/m^3 and 0.0496 kg/m^3 for 0.025 A and 0.026 kWh/m^3 and 0.0496 kg/m^3 for 0.05 A. Energy and electrode consumptions were calculated as 0.0327 kWh/m^3 and 0.0744 kg/m^{3}at 0.10 A and 90°C.

Boron and arsenic concentrations in Acep (GW-1) and Tülü (GW-2) borate open pits were 1020.5 µg As/L and 336.6 mg B/L, and 300.5 µg As/L and 226.7 mg B/L (Table 1). B concentration is very high in these mines because boron minerals are in contact with in natural waters. At 0.025, 0.05 and 0.10 A, effluent arsenic concentrations in the EC process were 7.2 µg/L at 60 min, 6.9 µg/L at 50 min and 7.1 µg/L at 30 min of EC time (Fig. 4b). Effluent B concentrations for 0.025, 0.05 and 0.10 A at 60 min were obtained as 333.1, 330.3 and 297.4 mg/L, respectively. Energy and electrode consumptions were 0.0465 kWh/m^3 and 0.0944 kg/m^3 at 90°C for 0.025 A, 0.0530 kWh/m^3 and 0.154 kg/m^3 at 150°C for 0.05 A, and 0.0511 kWh/m^3 and 0.179 kg/m^3 at 180°C for 0.10 A, respectively. As applied current was increased, electrode and energy consumptions were also increased but operating time decreased. On the other hand, effluent pH_f for 0.025, 0.05 and 0.10 A were 9.8, 10.2 and 10.8 at 60 min, respectively. Dissolved amount of Fe anodes increased by the increase in pH since more Fe was dissolved at high pH. However, it was thought that the removals from groundwater were achieved with precipitation with Fe-arsenic ions and adsorption. Ferric ions generated by electrochemical oxidation of Fe electrode may form monomeric species and polymeric hydroxyl iron complexes depending on the pH of the aqueous medium, which have strong affinity for dispersed particles as well as counter ions to cause coagulation. In addition, arsenic is usually strongly adsorbed by iron oxides such as amorphous Fe(OH)$_3$, hydrous ferric oxide (HFO) and goethite (FeOOH). Therefore, arsenic is removed by iron species either by compound formation or by surface complex adsorption or both [38].

$$4Fe \rightarrow 4Fe^{2+} + 8e^- \tag{1}$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \tag{2}$$

$$2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^- \tag{3}$$

When introducing air (or oxygen) to the process, Fe^{2+} is oxidized rapidly in bulk solution:

$$O_{2(g)} + 4Fe^{2+} + 2H_2O \rightarrow 4Fe^{3+} + 4OH^- \tag{4}$$

The applied current forces OH^- ion migration towards the anode, thus favouring ferric hydroxide formation [36–39]:

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_{3(S)} \tag{5}$$

The arsenic removal by co-precipitation results in that the OH^- positions in hydroxide are substituted by arsenic ions:

$$2FeOOH_{(S)} + H_2AsO_4^- \rightarrow (FeO)_2\,HAsO_4^- + H_2O + OH^- \tag{6}$$

$$3FeOOH_{(S)} + HAsO_4^{2-} \rightarrow (FeO)_3\,AsO_{4(S)}^- + H_2O + 2OH^- \tag{7}$$

Groundwater sample taken from Tülü boron open pit contained 300.5 µg/L of arsenic and 226.7 mg/L of boron (Table 1). Effluents arsenic concentrations after the EC process were 8.2 µg/L at 40 min for 0.025 A, 5.6 µg/L at 15 min for 0.05 A, and 7.8 µg/L at 10 min for 0.10 A (Fig. not depicted). In this case, energy and electrode consumptions were 0.0368 kWh/m^3 and 0.0511 kg/m^3 at 60°C for 0.025 A, 0.021 kWh/m^3 and 0.036 kg/m^3 at 45°C for 0.05 A, and 0.0205 kWh/m^3 and 0.045 kg/m^3 at 60°C for 0.10 A, respectively. Moreover, effluent pH_f for 0.025, 0.05 and 0.10 A at 40 min were 8.9, 8.6 and 8.5. Effluent B concentrations for 0.025, 0.05 and 0.10 A at the EC conditions were 223.2, 218.6, and 212 mg/L, respectively.

3.2. Studies on boron removal by ion exchange

Amberlite is a boron specific resin, and it offers very good selective ion exchange efficiency for boron. Amberlite IRA-743, an ion-exchange resin, manufactured by Rohm

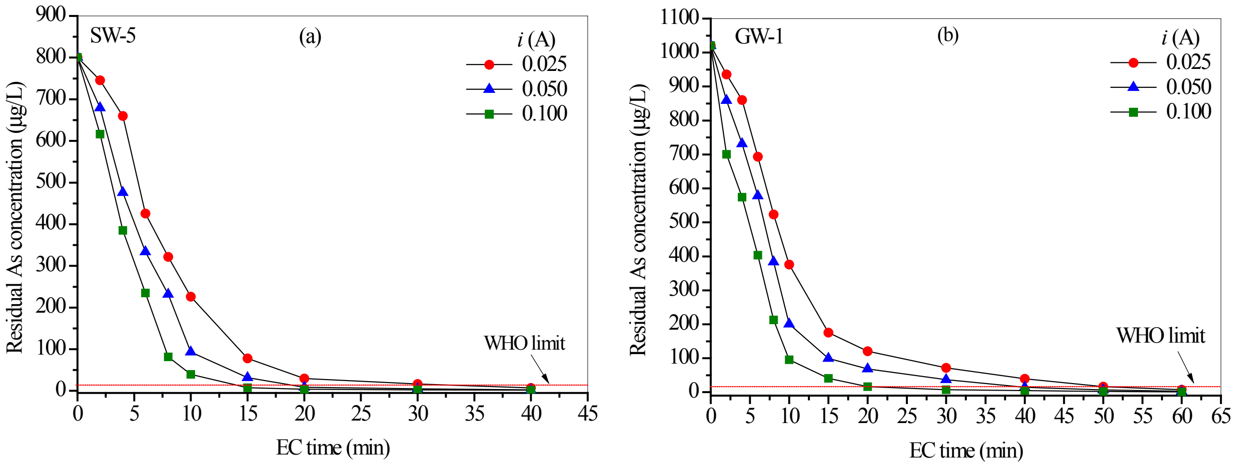

Fig. 4. Arsenic removal efficiencies for SW-5 and GW-1 at different applied currents in the EC process.

and Haas, has a macroporous matrix, on which N-methylglucamine functional groups are attached. Borate ions in solution are complexed with two sorbitol groups on the resin, and a proton is retained by a tertiary amine site that behaves as a weakly basic anion exchanger. In this study, As concentrations in the water samples were reduced to the required level set by the WHO (<10 µg/L) in the EC process using Fe plate anodes. The lowest energy and electrode consumptions from the above results were obtained at 0.025 A because values of the consumptions affected the operating cost of the EC process. After the filtration of samples (sludge from the EC) were treated for removal of B with Amberlite IRA-743 resin (0.025–3 g). B removal efficiencies for SW-1, SW-2, SW-3, SW-4, SW-5, GW-1 and GW-2 were 3.4, 4.2, 4.3, 4.2, 3.8, 1.04, and 1.6%. As the results indicated that the EC process was not successful to remove B from the sample efficiently (Table 1). Other important point is pH value of natural waters containing B. During the EC process, effluents pH values were observed to increase and this was an advantage to remove B from the sample using ion-exchange process using Amberlite IRA-743 resin at pH 8–11 which was the recommended value in an earlier report [54]. Therefore, no pH adjustments for removal of B were made after effluents collected from the EC process. Effluents pH values in the EC process were found to be 8–10. Effluents B concentrations (C_f, mg B/L) and adsorption capacities (q_e, mg B/g resin) at different resin dosages were presented in Tables 2 and Fig. 5. As the resin dosages were increased, concentrations of C_f were decreased but amount of B adsorbed per resin dose (g) was observed to decrease (Tables 2 and Fig. 5). In addition, boron absorption decreased as the initial boron concentration increased in water samples. Some literature results were reported with use of the resin in the following studies. Darwish et al. [54] investigated boron removal by Amberlite IRA743, and adsorption capacities were 3.67 and 5.41 mg/g for feed solution with initial boron concentrations of 1.5 and 5.0 g/L at the optimum conditions (resin dosage of 0.4 g/L, a pH of 8, 25°C, and ion-exchange time of 120 min, respectively. Boron adsorption capacity at different experimental conditions was calculated as 6.7 mg B/g resin by Xu and Jiang [59], and 7.5 mg B/g resin by Wei et al. [60]. The pH dependence of boron uptake was interpreted by taking into account the dissociation process of $B(OH)_3$ in aqueous solutions and formation of bidentate complex of borate ion with two N-methyl-D-glucamine groups of the resin. The resin's hydroxyl groups had higher affinity for $B(OH)_4^-$ ions comparing with $B(OH)_3$ species [54]. Boric acid at a pH lower than 7 is un dissociated as H_3BO_3 or $B(OH)_3$, but boron occurs as dissociated borate $B(OH)_4^-$. Therefore, many studies reported for the removal of boron was optimised at pH 9–9.5.

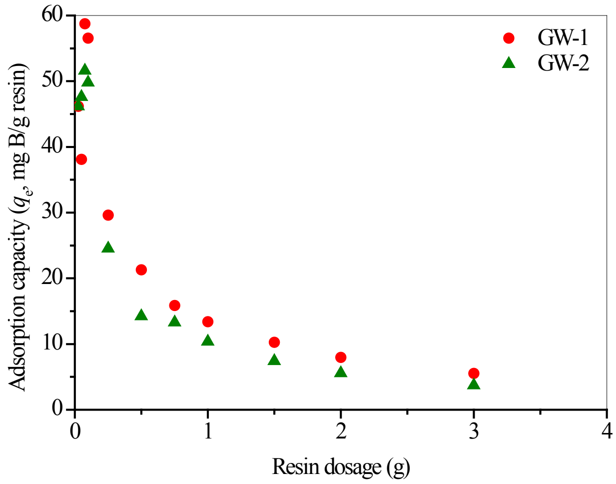

Fig. 5. Adsorption of boron from the groundwater samples at different resin dosages.

4. Conclusions

In this study, spring and groundwater samples from Bigadiç boron mine contained As and B areas were treated with EC process using Fe plate anodes. The removal efficiencies of arsenic with effluent concentrations of <10 µg/L from the samples at 0.025–0.10 A and 0–60 min were obtained as 97–99.9% at 2–16 min. As the operating time and current increased, the removal efficiency of arsenic was also increased. However, the removal efficiencies of B weren't successful in the EC process (1.0–4.3%). Final pH values were increased during the EC process which helped to increase the removal efficiency of B when the effluent

Table 2
Results of boron removal by Amberlite IRA-743 at different resin dosages

ws (g)	SW-1		SW-2		SW-3		SW-4		SW-5	
	C_f (mg/L)	q_e (mg/g)	C_f (mg/L)	q_e (mg/g)	C_f (mg/L)	q_e (mg/g)	C_f (mg/L)	q_e (mg/g)	C_f (mg/L)	q_e (mg/g)
0	13.87	0	5.9	0	26.2	0	9.1	0	90.11	0
0.025	6.32	15.1	1.3	9.2	8.1	36.2	3.6	11.0	82.10	23.1
0.050	2.4	11.47	0.2	5.7	2.2	24.0	1.1	8.0	70.40	23.3
0.075	0.35	9.01	0.01	3.9	0.4	17.2	0.24	5.9	64.97	19.1
0.100	0.01	6.93	0.001	2.9	0.1	13.1	0.05	4.5	59.53	17.1
0.250	0.01	2.77	0.001	1.2	0.001	5.2	0.01	1.8	37.59	11.2
0.500	0	1.39	0	0.59	0	2.6	0	0.9	8.62	8.5
0.750	0	0.92	0	0.39	0	1.8	0	0.61	0.56	6.2
1.000	0	0.69	0	0.30	0	1.3	0	0.46	0.02	4.7

was treated with ion exchange process since commercial boron removal resins are effective at pH8–11. A removal efficiency of 99–100% for B in the spring and groundwater samples after filtrated from the EC was achieved at a resin dosage of 0.75 g. As a result, the consecutive processes were found to be successful for removals of arsenic and boron from natural waters in the boron mining regions.

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