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Boron in geothermal energy: Sources, environmental impacts, and management in geothermal fluid

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ARTICLE INFO

Keywords: Geothermal energy Geothermal water Renewable energy Boron Water treatment Outflow water Pollution

ABSTRACT

The problem of hazardous chemicals in geothermal fluid is a critical environmental concern in geothermal energy developments. Boron is among the hazardous contaminants reported to be present at high concentrations in geothermal fluids in various countries. Poor management and inadequate treatment of geothermal fluids can release excessive boron to the environment that has toxic effects on plants, humans, and animals. Despite the importance of boron management in geothermal fluid, limited and fragmented resources exist that provide a comprehensive understanding of its sources, transport and fate, and the treatment strategies in geothermal energy context. This paper presents the first critical review from a systematic and comprehensive review on different aspects of boron in geothermal fluid including its generation, sources, toxicity, ranges and the management approaches and treatment technologies.

Our research highlights the origin of boron in geothermal water to be mainly from historical water-rock interactions and magmatic intrusion. Excessive concentrations of boron in geothermal fluids have been reported (over 500 mg/L in some case studies). Our review indicated that possible boron contamination in geothermal sites are mostly due to flawed construction of production/re-injection wells and uncontrolled discharge of geothermal water to surface water. The dominancy of non-ionic H_3BO_3 species makes the selection of the suitable treatment method for geothermal waters limited. Combining boron selective resins and membrane technologies, hybrid systems have provided effluents suitable for irrigation. However, their high energy consumption and course structure of boron selective resins encourage further research to develop cost-effective and environmentally friendly alternatives.

Abbreviations: AGMD, Air Gap Membrane Distillation; Al, Aluminium; As, Arsenic; B, Boron; BSR, Boron Selective Resin; BWRO, Brackish Water Reverse Osmosis; CHT, Calcined Hydrotalcite; EBRD, European Bank for Reconstruction and Development; EDI, Electro-Deionization; F, Fluoride; F, Iron; FO, Forward Osmosis; GE, Geothermal Energy; GW, Geothermal Water; HT, Hydrotalcite; µm, Micrometer; MD, Membrane Desalination; mg/L, Milligram Per Littre; mg/kg, Milligram Per Kilogram; mM, Milli Molar; NMDG, N-methyl-d-glucamine; NF, Nano Filtration; OP, Operation Pressure; RO, Reverse Osmosis; Sb, Antimony; SWRO, Sea Water Reverse Osmosis; T, Temperature; UF, Ultra Filtration; WHO, World Health Organization.

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1. Introduction

 ${\rm CO}_2$ reduction can be achieved through the implementation of five key strategic technologies. These include renewable energy (32% contribution), increased energy efficiency (32%), carbon capture storage (15%), nuclear (11%) and fuel switching (10%) [1]. Renewable energies are environmentally friendly, considered to be non-polluting, and have lower operation and management costs. Among renewable energies, geothermal energy (GE) has attracted significant attention with potential electricity generation of 1400 TWh per year by 2050 (\sim 3.5% of global energy production). Such a contribution would reduce ${\rm CO}_2$ emissions by approximately 800 Mt per year [2].

Despite being considered as a clean source of energy, GE production could pose some environmental problems if not managed properly. Geothermal fluid management and possible water pollution caused by them is one of the most important environmental challenges associated with GE production [3-5]. This is due to the fact that the geothermal fluid (outflow water) may contain high concentrations of different hazardous chemicals [2,5–7]. Among water contaminants, boron (B) is one of the important chemicals that can be found in the geothermal fluid. B commonly presents at high concentrations in geothermal fluids, usually attributed to the leaching from the host rock and magmatic intrusion [8]. The contamination of waters and soils with discharged B-rich geothermal fluid in areas adjacent to geothermal sites has resulted from large-scale exploration and exploitation of GE. For instance, substantial discharge of geothermal fluids has raised B concentrations in the rivers in two Tibetan geothermal areas (Yangbajing and Yangyi) up to 3.8 mg/L and 0.7 mg/L, respectively [9,10]. Therefore, geothermal fluids produced for energy production or any other purposes should be re-injected back into the geothermal reservoir or treated before the discharge to water resources. On the other hand, water demands by different sectors have caused the baseline of water stress levels to shift to severe conditions where exceed the capacity of freshwater resources [11]. This has resulted in a paradigm shift in relation to water resource management by exploring the potential reuse of wastewaters. The geothermal wastewater reuse for agricultural purposes has attracted

attention in various regions of the world [12–14]. To use geothermal water (GW) for irrigation, B concentration should be reduced to lower than 1 mg/L for many sensitive agricultural products. Furthermore, B is used as a raw material for several industries, including the aircraft industry, aerospace, electronics, military vehicles, nuclear energy, fuel in fuel-cells cars, agriculture, and the glass industry. This makes B recovery from GWs to be an option for its management in GE [15,16].

Despite the importance of the issue, no study has been comprehensively assessed B in GWs, and data on B sources, impact, and management (treatment and recovery) is clustered in the literature. To fill this gap, the current critical review provides a comprehensive overview of B in geothermal fluids all around the world.

We have summarized for the first time data in the literature on sources and ranges of B in different geothermal fluids, mechanism of water pollution by geothermal fluids, regulation, B toxicity on various agricultural/horticultural products, and recently applied technologies on B treatment and recovery from GWs. Next, combining geochemical analysis of geothermal fluids and analyzing effectiveness of various current technologies in B treatment of geothermal fluids, we identified current challenges and introduced the future perspective on managing B in GE production sites. Fig. 1 summarizes our method in conducting the state-of-the-art literature review on managing boron in GE production site

2. Water contamination

2.1. Contaminants of concerns

B in geothermal fluids is the focus of this review. However, it is noted that a wide range of chemicals is present in geothermal fluid. The geothermal fluid composition is controlled by processes that mainly depend on the geological setting of the region, including the type of host rock, temperature, boiling and mixing process, and addition of vapour and volcanic gases into thermal waters [17–20]. GWs of Western Anatolia, Turkey which is an example of the complex system, contain arsenic (As), boron (B), antimony (Sb), and manganese (Mn) due to the specific

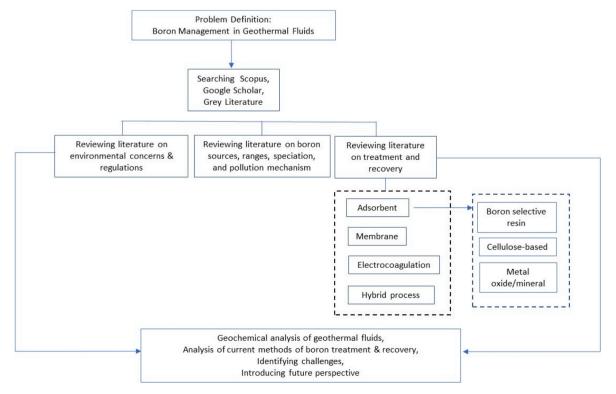


Fig. 1. The method of conducting the current state-of-the-art review.

geological characteristics of the region that form minerals containing these elements. In this region, the high temperature and pressure in deep reservoirs that are cut by geological fault lines and close active magma layers enhance the dissolution of minerals in GWs through rock-water interaction [2,21–23]. The presence of As, B, Mn, and fluoride (F) at concerning concentrations has been reported in GWs of northern Mexico with leaking potential to adjacent groundwater [24]. Considering such potential groundwater contamination [25], studied the soil retention capacity for As, B, and Pb in the vicinity of Cerro Prieto geothermal plant in northern Mexico and reported that B is a major concern for groundwater contamination due to poor retention of the studied soil. In GWs of Tibet, high concentrations of As, B, and F generated through fluid-rock interaction have also been reported as the main contaminants along with Cd, Li, and molybdenum (Mo) have been traced as other concerning contaminants [26].

2.2. Mechanism of pollution

The contamination of water resources with heavy metals sourcing from GE has been reported to be mainly due to flawed well construction, faulty re-injection applications, and discharge of untreated spent geothermal fluids to surface waters [2,27,28].

Fig. 2 depicts a conceptual model for the situations when flawed well construction of either production or re-injection wells or both can lead to groundwater contamination by geothermal fluids. As shown, the filter zone is not properly situated by faulty construction of both production and re-injection wells, so the geothermal fluids are not isolated from shallow groundwater. In addition, geothermal fluids could corrode well casings and make them ineffective in containing geothermal fluids leading to geothermal fluids leakage to cold groundwater [28].

The groundwater contamination caused by GE production has been reported in geothermal plants in Balcova and Alaşehir region in Western Turkey, and Yangbajain in Tibet, China. In all the three regions, As and B were reported as the main groundwater pollutants with Sb and F were also listed as groundwater contamination in Balcova and Yangbajain, respectively [9,29]. Similar faulty geothermal production practices were deemed as one of the two main potential sources along with geological formations for high As (up to 729.3 μ g/m³) and B (up to 3.94 mg/L) values measured in groundwater boreholes around Germencik and Sarayköy in Gediz and Büyük Menderes basins, Western Turkey [30].

Surface water contamination by uncontrolled discharges of GWs has also been reported in many regions of the world. For example,

discharging GWs of Yangyi to Loulang River, China has led to increases of As, B, Li, and SO_4^{2-} leading to As and B concentrations higher than standards for drinking water [10]. Discharging untreated GWs of Yangbajain geothermal plant to Zangbo river, China led to As, B, and F increases in the river to 0.25, 3.5, and 1.4 mg/L, respectively [9]. The untreated geothermal fluids discharge was reported as the source of high B concentrations (10–50 mg/L) in Germencik and Buharkent areas in Büyük Menderes basin, Western Turkey [30].

3. Boron: environmental concerns and regulation

B is a micronutrient essential for plant, animal and human life. In plants, it plays an important role in stabilizing cell walls, reproductive growth and stimulation, seed quality, and biosynthesis [31]. In humans, B participates in the body's metabolism, so insufficient B intake can lead to abnormal bone growth, low hormone concentrations, increased calcium levels, and shifts in micromineral status [32]. For animals, it has been reported that B deprivation affects the fertility of zebrafish, trout, and frogs [33].

Despite being an essential microelement, excessive B intake has toxic effects on plants, humans, and animals. B toxicity in plants is considered as one of the important potential environmental impacts of GE production [5]. In addition, B containing GW is considered as a potential water resource for irrigation [13,14,34] making the knowledge of B toxic effects on plants of great importance. Common responses of plants to elevated B concentrations in irrigation water include poor root development, higher oxidative stress due to increased reactive oxygen species, and impaired photosynthesis [31]. B tolerance varies among various agricultural products from below 0.5 mg/L for very sensitive species (e.g., lemon, blackberry) to 6-15 mg/L for very tolerant ones (e. g., cotton, asparagus) (Fig. 3). The B limits in irrigation water are determined by the sensitivity of the crop and soil condition [35]. Therefore, the target of less than 1 mg/L has been considered as the required treatment level for B by many studies focusing on GW treatment in the regions with sensitive agricultural products [14,35].

Various B toxic effects on humans have been reported, including adverse effects on the fetus during pregnancy, kidney damage, anorexia, diarrhea, and weight loss [32]. The World Health Organization (WHO) set the daily tolerable intake of 0.2 mg B/kg body weight. Considering this tolerable intake and assuming a consumption of 2 L water per day by a person with the bodyweight of 60 kg, WHO suggests a guideline of 2.4 mg B/L in drinking water [38]. Various jurisdictions consider either

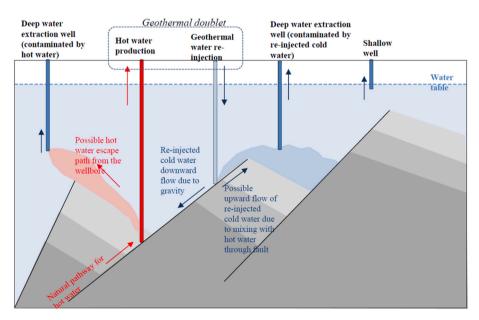


Fig. 2. Schematic of groundwater contamination by geothermal energy production (Modified based on [28].

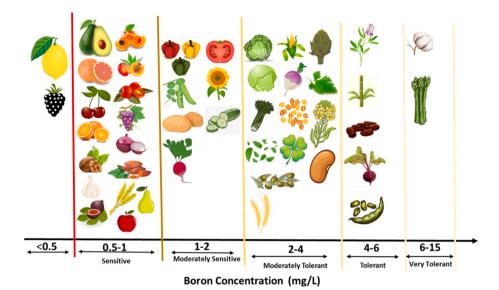


Fig. 3. Boron Sensitivity of different crops based on [36,37].

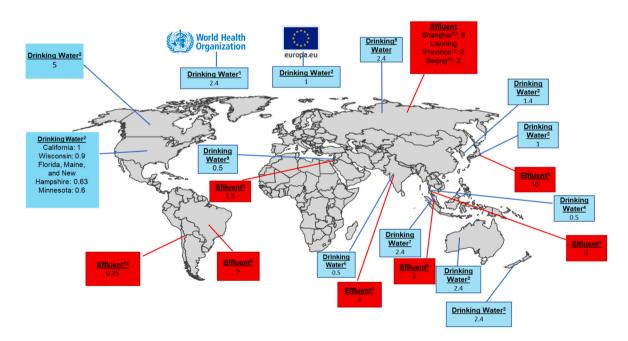
stricter or softer limits for B in drinking water all around the world. For instance, European Union considers a B limit of 1 mg/L in drinking water while the Canadian government allows B concentration as high as 5 mg/L. The regulations set by various jurisdictions for B concentration in drinking water and allowable values for wastewater discharge (effluent) to receptor water bodies [38–49] are listed in Fig. 4.

4. Boron sources, ranges, and speciation in geothermal fluids

4.1. Sources and ranges

High B and sulphate (SO_4^{2-}) concentrations in GW suggest that it is heated by magmatic sources [50]. Due to its high solubility, leaching from the host rock reservoir is considered as the main B source in GWs.

Therefore, geothermal fluid-rock interactions are considered as the important B source for many geothermal systems hosted by high-B containing rocks, including Taupo Volcanic Zone (New Zealand) [51], Cimino-Vico (Italy) [52], and Nesjavellir (Iceland) [53]. Tourmaline-bearing granite, gneisses and schists with tourmaline, biotite, and muscovite, Mesozoic rock, and flysch are reported as high-B containing geothermal waste rock [8,52,54]. In addition to the leaching from host rock, the intrusion of magmatic fluid may be another important source of B in geothermal systems with a magmatic heat source, such as Vulcano (Italy) [55], Los Humeros (Mexico) [56], and Milos Island (Greece) [57]. High B concentrations (15–100 mg/L) have been recorded in the brine of high-temperature geothermal systems such as Kızıldere, Alaşehir fields (Turkey) and Salton Sea (US), above 100 mg/L for Java (Indonesia) [45,58,59], and above 500 mg/L for Tibet,



Notes: the references where boron limits are extracted from are listed bellow:

1. [38]; 2. [39]; 3. [40]; 4. [41]; 5. [42]; 6. [43]; 7. [44]; 8. [45]; 9. [46]; 10. [47]; 11. [48]; 12. [48]; 13. [49].

Fig. 4. Boron limits for drinking water and discharge to water bodies set by various regulators all around the world (mg/L).

China [60]. Fig. 5 summarized some geochemical characteristics of GWs all around the world discussed in the literature.

In Turkey, geothermal sites are located in Western Anatolia (mostly high temperature) and Central Anatolia (low temperature). B occurrence in geothermal sites of Western Anatolia is explained by water-rock interactions and the thick oceanic sediment layer at the bottom of Anatolia which has resulted in B-containing mineralization (such as tourmaline, biotite, and muscovite) in rocks with typically low B contents such as gneisses and schists, hydrothermal mineralization, and geothermal circulation during the pegmatitic-pneumatolytic phase that enables the enrichment of B minerals in Western Anatolia [54]. Various B concentration ranges have been reported in GWs of the region from 4.2 to 7.5 mg/L in Gölemezli geothermal field [60] to 76.7-104 mg/L in Alaşehir [50] with the lower range was attributed to not reaching re-equilibrium, likely due to mixing with cold water during their pathway. Leachate from host rock through water-rock interaction and ion exchange reactions is suggested as the main process which determines chemical constituents of GW including B concentration, while sea water intrusion is considered as the B source on some occasions such as Sultanhisar [50, 61-63]. The reported pH of GW and reservoir temperature (estimated using various geothermometers) ranges varied from 5.9 to 7.6 (Na-SO₄, Ca-SO₄, and Ca-HCO₃ types) and 130-210 °C in a geothermal plant in Gölemezli to 7.1-8.5 (Na-HCO₃ water type) and 229-259 °C in another one in Alaşehir with Eh was only reported as -309 to 20.5 mV in Alaşehir [50,61]. Lower B concentrations ranged from 1.97 to 2.66 mg/L with pH of 6.6-6.9 have been reported in low-temperature geothermal sites (reservoir temperature of 68–105 $^{\circ}$ C) in Kavak geothermal field in Seydisehir, Central Anatolia [64].

In China, high B containing GWs are distributed in the Tibet Autonomous Region. Tibet is an important part of the Mediterranean-Himalayas geothermal belt where possesses hydrothermal systems with reservoir temperatures above 150 °C [65]. [8] categorized the hydrothermal waters in Tibet into four groups of acid low-B waters, acid high-B waters, neutral/alkaline low-B waters, and neutral/alkaline high-B waters. Acidic low-B waters collected from Daggyai geothermal area were found to have a B concentration range of 1.1–1.2 mg/L, a pH range of 3–4.5, and classified as high and very low chloride

(Ca-Na-SO₄) type water. These acidic waters are essentially locally-perched groundwater heated by geothermal vapour separated from flashed deep geothermal fluids [66]. Acid high-B waters with 90.9 mg B/L were collected from the Semi geothermal area, hydro-chemically classified as Ca-Na-SO₄-Cl. These GWs could be originated from the mixing of steam-heated and neutral Cl-rich waters. Neutral/alkaline high-B waters with pH = 7.7 were categorized as Na-Cl and Na-H-CO₃-Cl waters. The co-existence of acid SO₄²-rich, neutral Cl-rich, and alkaline HCO3-rich GWs suggested the occurrence of magmatic heat sources in the Daggyai and Semi regions as suggested by Ref. [67]. In addition, the close Na-K temperatures of neutral/alkaline high-B GWs indicates that they likely evolved from deep geothermal fluid fully equilibrated with Na+, K+, and Mg2+ bearing reservoir minerals. Therefore, a probable B source for the neutral/alkaline high-B GWs is magmatic fluid. However, higher Ca²⁺ and comparable Cl⁻, HCO₃, and SO₄²⁻ along with much lower concentrations of As, Li, Rb, and Cs in alkaline/neutral low-B GWs in Quzhuomu suggest that they are non-magmatic and received B from leaching B-bearing reservoir host rocks, i.e. tourmaline-bearing granite.

High-temperature geothermal systems (T > 250) in New Zealand are found in Taupo Volcanic Zone (TVZ) and Ngawha in North Island, while moderate to low-temperature geothermal systems are widely scattered. High B (17.5–82.1 mg/L) were reported in GWs of TVZ ranging with a positive correlation between Na and B suggesting that aqueous B concentration is controlled by fluid-rock interaction [51]. In addition, low B isotope (8^{11} B) values (-6.7 to -1.92%) and low Cl/B ratio (52) implied the volcanic origin of GWs with no significant marine input [51].

[52] reported a B concentration range of 0.06-1.15 mg/L in the GWs of the low-enthalpy geothermal system of Cimino-Vico Volcanic District, Italy. GWs are classified as SO_4^{2-} rich waters with SO_4^{2-} /HCO ratio range of 0.3-1.6. It is suggested that B in GWs of the region is originated from dissolution of the borosilicate minerals making up the Ligurid units. Reservoir rock of the geothermal system consists of flysch rock with underlying Mesozoic rock. Flysch rocks are naturally rich in B [68] and could have been further enriched with B in this region as separated B from underlying Mesozoic could be redeposited into secondary minerals like tourmaline during probable high-enthalpy.

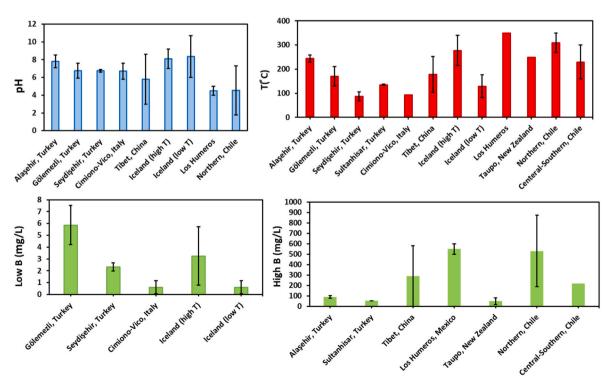


Fig. 5. Geochemical characteristics of geothermal water all around the world.

[53] studied B in GWs of high and low-temperature geothermal systems in Iceland and reported ranges of 0.79–5.71 and 0.06–1.16 mg/L for high and low-temperature geothermal systems, respectively, and correlated with the geothermal fluid's temperature. Interaction with basalt (host rock) was suggested as the B source in the geothermal fluid, and mixing with sea water was suggested as the reason for the lower B concentration and temperature of the low-temperature geothermal fluids.

[55] implemented a 3-level model in a thermodynamic code, HSC-7 [69], to explain high B concentration in geothermal fluids of Mexico. The suggested model comprised: 1) immature highly acidic brine at depth which boiled at $T\sim350\,^{\circ}\text{C}$ and produced HCl-bearing vapour with high B; 2) partial condensation of the produced vapour, followed by interaction of the resultant water with rock and neutralization; 3) formation of a shallow water-dominated aquifer above a lithologic low-permeability boundary. Using the model, they suggested that the acidic brine (pH = 3–5) with >500 mg B/kg beneath the main productive reservoir was the B source in geothermal fluids. This acidic brine resulted from magmatic fluid and leaching of wall led to average B concentrations of 150 and 5000 mg/kg in geothermal fluid (water + steam) and separated waters, respectively.

High temperature geothermal systems in Chile (and other Andean countries) are in strong spatial and genetic relationship with the active volcanism. This magmatic activity is mainly controlled by the almost continuous subduction of the Nazca Plate under continental South American Plate, present since Jurassic times [70]. The geothermal system of the region is divided into two zones: Northern and Central-Southern geothermal zones. In the Northern geothermal zone, Cerro Pabellón geothermal system host the first (and the only one as of writing this article) geothermal power plant running in South America [71]. provides the first geochemical data of the geothermal fluids from Cerro Pabellón production wells, reporting B values of 258-343 mg/L, with pH of 6.74-7.12. High B and Cl contents in the geothermal fluids are attributed to intense leaching from host rock in a long living system without almost surface discharge. Higher B values (503-1020 mg/L) resulted from intense leaching from host rock were also reported by Ref. [72] for the GWs (pH = 1.76-7.30) of Puchuldiza geothermal site with the reservoir temperature range of 270-350 °C, located in the region. For the Central-Southern geothermal zone in Chile [73], reported B values of 219 mg/kg from a production well (T = 160–300 $^{\circ}$ C) from the ex-Tolhuaca geothermal project. The B source in the GWs of the system was attributed to leaching from host rock coupled with the high magmatic diversity of volcanism in this segment of the Andean Cordillera [74].

4.2. Boron speciation

The main B species in aqueous solution is boric acid $(H_3BO_3/B(OH)_3)$ which is a weak acid with pK_a value of 9.2 and its conjugate base $(B(OH)_4)$ that predominate in alkaline condition $(Eq.\ (1))$. With increasing the total B concentration, polyborates are formed starting from 220 mg B/L $(20\ mM$ as boric acid) [75]. The formation of polyborates is discussed in chemical reactions 2a-d [76]. As dissociation of H_3BO_3 occurs at pH=9.2; this weak acid is the most dominant B species at lower pH. Increasing pH results in shifting reaction 1 to the right, which increases $B(OH)_4$. Thus, the most important factors determining B species in aqueous solutions is pH and total B concentrations. As shown in Fig. 4, GWs usually have pH ranges below 9.2 and B concentration ranges less than 220 mg/L. Therefore, H_3BO_3 should be the dominant B species in most GWs around the world apart from some places with high total B concentration (e.g., China, Mexico) that may expect considerable polyborates in GWs.

$$B(OH)_3 + H_2O \Rightarrow B(OH)_4 + H^+ K_a = 10^{-9.2}$$
 (1)

$$3B(OH)_3 \Rightarrow B_3O_3(OH)_4^7 + 2H_2O + H^+ K_{P1} = 10^{-7.29}$$
 (2a)

$$5B(OH)_3 \Rightarrow B_5O_6 (OH)_4^- + 5H_2O + H^+ K_{P2} = 10^{-6.77}$$
 (2b)

$$4B(OH)_3 \Rightarrow B4O5(OH)_4^{2-} + 3H_2O + H^+ K_{P3} = 10^{-14.5}$$
 (2c)

$$3B(OH)_3 \Rightarrow B3O3(OH)_5^{2-} + H_2O + 2H^+ K_{P4} = 10^{-16.3}$$
 (2d)

Temperature and F concentration are the other parameters that could play role in B speciation in GWs. For GW with a high total B concentration, the considerable polyborates and $B(OH)_4^-$ concentrations (up to 36.7 and 38%, respectively) has been predicted by geochemical modelling only at relatively high temperature (over 87 °C), while B (OH) $_3$ has been the dominant species in a temperature range of 36.7–87 °C [8]. At high F/B (=10), B more likely complexes with F forming BFn(OH) $_4$ -n [8,77]. However, a low percentage of fluoroborate compounds (<0.1%) has been predicted in both high and low B containing GWs with high F concentrations based on geochemical modelling [8].

5. Treatment and recovery

The experience of B extraction from geothermal fluids is back to 18th century in Larderello geothermal system in Italy well before the usage of the heat for power generation where B was recovered from geothermal fluid using crystallization and concentration of boric acid by wood fire [78-80]. Until the shortage of wood in the region and addition the cost of its supply caused by transportation which affected the profitability, geothermal fluid was only employed as raw material for B production [80]. The idea of capturing steam and utilizing its heat to concentrate boric acid to overcome the problem of wood shortage, opened the way for utilizing geothermal heat as a driving force in reciprocating machines which eventually led to electric energy production from geothermal fluid for the first time in the world in 1904 [80]. Electricity production also provided a favorable condition for B recovery from geothermal fluid in Larderello by adaption of a thermal cycle with indirect steam utilization designed to protect turbine blades from chemical attacks of natural steam, which made concentrated boric acid production feasible [80]. Despite the great potential of B recovery known for a long time, internationally B extraction has focused on environmental remediation (i.e., geothermal fluid treatment), not economic recovery [81]. While partial condensation as a concentration method has been used in Larderello geothermal system, sorption techniques widely used for B treatment are also the method of choice for boron extraction [82]. However, the focus of studies has been on the B separation from the geothermal fluid with limited discussion on its recovery and rates through adsorbent regeneration. The adsorption of boron from geothermal fluid and its recovery in geothermal fluid is broadly discussed in Section 5.1.

The treatment technologies applied to GE can be categorized into four main groups, including adsorption, membrane technologies, hybrid systems which use the first two technology together, and electrocoagulation in which adsorption is the main B removal mechanism (Fig. 6). Adsorption is deemed to be the most effective method for the B treatment in aqueous solutions, given its simplicity and effectiveness even at low B concentrations [83]. The most common adsorbents have functionalized groups such as N-methyl-d-glucamine (NMDG) or metal oxides/hydroxides on their surfaces which can remove B from GW through chelation and surface complexation [84]. Membrane technologies mostly relies on size exclusion [14], whereas electrocoagulation uses adsorption of boric acid (H₃BO₃) on the surface of metal hydroxide (usually Al) generated in situ from dissolution of the metal in the anode.

5.1. Adsorption

Boric acid (H₃BO₃) has shown a great affinity to polyols through chelating mechanism [85]. This had led to the development of adsorbents grafted by functional groups rich in vicinal diols. At the time of

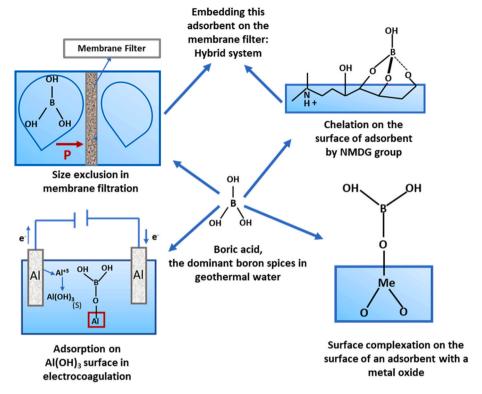


Fig. 6. Main technologies applied to B treatment of geothermal waters.

writing, N-methyl-d-glucamine (NMDG) has been the most adapted functional group in two commercialized adsorbents, including B selective resins (BSRs) and fibers. Macroporous Tpolystyrene and cellulose are the matrix of the BSR and fiber adsorbents. In the following sections, the application of BSRs (and other types of resins) to the B treatment of GW are first discussed followed by fibers and other used adsorbents in previous studies.

5.1.1. Resin

BSRs have initially been recognized as the most important adsorbent for aqueous B removal and even the most common technology for aqueous B treatment according to literature [86–88]. Commercially available BSRs functionalized by NMDG, including CRB 01/02/03, Purolite 108, and Dowex (XUS43594.00) have widely been used for B treatment in GWs; especially in geothermal power plants in Turkey and Greece resulted in a broad range of B sorption capacity (3.4–15.6 mg/L) with the minimum obtained by Purolite 108 for an initial B of 3.5 mg/L

 Table 1

 Boron removal from geothermal water by various resins.

Resin type	Geothermal water resource	Initial concentration (mg/L)	Total sorption capacity (mg/g)	Sorption efficiency (%)	Reference
Diaion CRB 02	Kızıldere/Denizli/Turkey	30	5.98	90.0	[95]
Purolite S 108			4.52	93.3	
Diaion CRB 01	Kızıldere/Denizli/Turkey	18–20	4.86	>90.0	[96]
Diaion CRB 02			5.09		
Purolite S 108			3.57		
Diaion CRB 02	Balçova/İzmir/Turkey	12–13 (well 1)	5.02	>90.0	[92]
Dowex (XUS43594.00)		8.5–9.5 (well 2)	7.08		
Lewatit MK 51	Balçova/İzmir/Turkey	10.7	7.01	>90.0	[92]
Calcined hydrotalcite, KW-1000	Hachimantai/Japan	235	aN.A.	97.0	[97]
Vionit AS-116	northwestern Romania	59.45 (well no. 4058)	^b 30.48	^a N.A.	[89]
		95.10 (well no. 4667)	^b 25.00		
Diaion CRB 03	GW/Hachoubaru region/Kyushu	33.9	5.73	>95.0	[90]
Lewatit MK 51	Island/Japan		3.49		
Porous poly (GMA-co-EDM) resin containing NMDG	Balçova/İzmir/Turkey	11.0	2.59	94.0	[98]
poly(N-(4-vinylbenzyl)-N-methyl-D-	Balçova/İzmir/Turkey	10.5-10.9	^a N.A.	98.0	[99]
glucamine)				85.0	
Diaion CRB 02					
Diaion CRB 02	Balçova/İzmir/Turkey	10.0-11.0	7.55	95.0	[90]
Diaion CRB 05	•		15.60		
Chelest Fiber GRY-HW			13.05		
Purolite S 108	Anthemountas basin Northern Greece	3.5	3.4	^a N.A.	[100]

^a Not available.

 $^{^{\}rm b}\,$ mg/mL resin.

[89,90] and the maximum obtained by CRB/05 for an initial B of 10–11 mg/L [86]. Other types of commercially available resins such as Vionit AS-116, Porous poly (GMA-co-EDM) (functionalized with NMDG groups), and Lewatit MK 51 (functionalized with polyhydroxyl groups) have also been studied for B treatment in GWs in Turkey, Romania, and Japan which have given comparable results with those of BSRs functionalized with NMDG. For instance, Lewatit MK 51 gave a sorption capacity range from 3.49 mg/g in Hachoubaru region, Japan [91] to 7.01 mg/g in Izmir, Turkey [92].

Table 1 summarizes studies on B treatment in GWs using various ion exchange resins. As it discusses, good sorption capacity (3.4-15.6 mg/g) and high removal efficiency (90-98%) have been reported for various GW containing 3.5–95.1 mg B/L. Limited discussions exist on the effects of different parameters on B treatment in GWs using resins. In general, the current commercial BSRs have shown negligible pH-dependency (at pH = 7–10) in B removal from high salinity groundwaters because the chelating process (their main sorption mechanism) is independent from pH [92]. Lower sorption capacities of BSRs have been reported at pH = 10.5 in synthetic wastewater containing 5 mg B/L [39] likely due to the increase of hydroxyl anions competing with borate for the sorption side. On the other hand, higher sorption capacities have been reported in lower temperatures (25 °C) compared to higher ones (70 °C) in B removal from high salinity groundwater [93], while temperatures below 25 °C could decrease B sorption likely due the decrease in Brownian motion of B species in the solution resulting in the decrease of B binding with functional groups [39].

Resin particle sizes and feed flow rates are considered as important parameters in B removal from GWs (with 10–11 mg B/L) by BSRs. Smaller particles and lower flow rates showed higher B sorption due to their larger available surface areas and higher contact time of B and sorption sites, respectively [94]. In short operation time of 2 h, 45–125 μm and 0.5 mL/min were found as optimum resin particle sizes and GW flow rate for B removal by Diaion CRB02, and in long operation time of 24 h, resin particle sizes of <20 μm and GW flow rate of 1 mL/min for B removal by Dowex (XUS 43594.00) resin were found as the optimum parameters by Ref. [94].

While a recent study by Ref. [101] discusses that the adverse effect of phenol on B removal using Vionit AS-116 resin, it is expected that the presence of other salt ions in GWs do not affect B removal by BSRs as shown by Ref. [39] in B removal by Amberlite IRA743 resin using synthetic wastewater containing Na $^+$, Mg $^{2+}$, Cl $^-$, and SO $_4^{2-}$. Similar selectivity of B by BSRs such as Diaion CRB 03 and Diaion CRB05 was shown by Ref. [102] testing B removal form synthetic wastewater containing Li $^+$, Mg $^{2+}$, K $^+$ with adsorption of Mg $^{2+}$ at pH = 10.

Despite effectiveness, many drawbacks of BSRs for aqueous B treatment including limited surface area, hydrophobicity of the polystyrene, unordered pore structure, poor chemical and thermal stability, high cost of regeneration, make research to find more effective adsorbent necessary [93,94,103]. In addition, BSRs are recommended only for low B-containing wastewaters (e.g., <100 mg/L) to avoid frequent regeneration processes [84]. Recent research aimed at finding alternative B adsorbents has focused on developing matrices which improve hydrophilicity and maximize specific surface area, and utilizing functional groups other than NMDG [84]. These research studies have been resulted in developing cellulose-based fibers, clay-based, and metal oxide-based adsorbents of which those have been used for GW treatment will be discussed in the following sections.

5.1.2. Cellulose based adsorbent

The mechanism of adsorption on cellulosed-based adsorbent with NMDG functional group is as those of BSRs with the difference that the matrix structure is cellulose which has faster adsorption kinetic [102]. The only commercially available cellulose-based B-specific adsorbent is Chelest Fiber GRY-HW [84] that has been used for the treatment of GWs. The performance of Chelest fiber in B removal of GWs of Izmir, Turkey (B = 10-11 mg/L) has been compared with the commercially available

BSRs of Diaion CRB 02 and 05. The Chelest Fiber GRY-HW (18.52 mg/g) has shown higher B sorption capacity compared to Diaion CRB02 (13.7 mg/g) and CRB 05 (17.45 mg/g) in a batch experiment of B treatment of GW after 24 h [79]. The higher sorption capacity of Chelest Fiber can be explained by non-porous structure of the Fiber which locates functional groups on its surface eliminating the need of diffusion into particle pores in BSRs. However, Chelest Fiber (6.05 mg/g) showed lower sorption capacity than Diaion CRB 05 (11.22 mg/g) but still higher than Diaion CRB 02 (5.31 mg/g) in a column test with higher regeneration rate (89%). In another study [104], could increase sorption capacity of Chelest Fiber to 13.477 mg/g in a column test ran at speed velocity (SV) of 15 h^{-1} and concluded that a decrease in flowrate increases the longevity of the column by increasing both breakthrough and saturation time.

5.1.3. Metal oxides/minerals

Metal oxides and clay minerals have been also used as adsorbents for B treatment of GWs. The original hypothesis behind metal oxide-based adsorbents is that the hydroxyl groups on the hydrous surface of metal (hydro)oxides can form borate esters like chelating functional groups (Fig. 7). According to this hypothesis [105], studied the feasibility of B removal by steel and iron slags in sequence for treatment of GW of Los Humeros geothermal field collected from re-injection wells. Using both steel and iron slags (solidified and stabilized by commercial cement in 2/3 ratio) in sequence, they obtained an overall sorption capacity of 1.99 mg/g with an equilibrium time of 4 h at room temperature and pH = 9, which led to a decrease of an initial B concentration of 580 to 18 mg/L (96.9% removal) by steel stag and further decrease to 10.6 mg/L (40.5% removal) by iron slag. The low surface capacity and the high B removal achieved did not support the hypothesis of adsorption on the surface of metal oxides in this study. Thus, the sorption mechanism was explained as dissolution of iron, calcium, and magnesium-containing minerals in the slag and reprecipitation of insoluble minerals on the surface of slag captured B in their structure.

Hydrotalcite-like (HT) compounds are an important class of anion clays with a crystal structure comprised of brucite-like sheets [Mg (OH)₂], which have been scarcely investigated in the B treatment of GWs in their original form and calcination products (CHT). The mechanism of B sorption on HT and CHT is explained by their structure and functional metal oxides on their surfaces. The partial substitution of a trivalent metal ion for the divalent one in the HTs' structure induces a positive charge to its layers giving it the ability of adsorbing various anion including $B(OH)_4$. Furthermore, the calcination process leads to the formation of functional metal oxides of MgO and Al_2O_3 on the surface of CHT, which enhances B sorption through adsorption on Mg–Al oxides. The adsorption of B on the surface of metal oxides through forming

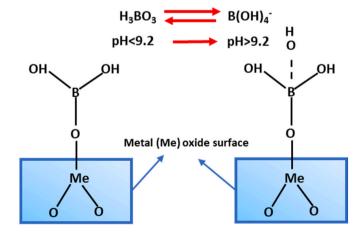


Fig. 7. Representative mechanism of boron adsorption on the surface of metal oxides [83,106].

Metal-B-O has been also demonstrated by Chen who studied B removal from water using magnetic magnetite (Fe $_3$ O $_4$). Moreover, the reconstructed structure of CHT allows B to intercalate into hydrotalcite layers due to the memory effect leading to an enhanced B removal from solution [26]. It has also been reported that HT and CHT could increase the pH of the solution up to 8.5 and 12.5, respectively, due to releasing OH⁻ [97]. Thus, the better performance of CHT in B removal can be attributed to dissociation of H_3BO_3 to $B(OH)_4$ followed by electrostatic sorption of $B(OH)_4$ on the positively charged surface of CHT.

[97] reported a B decrease in GW of Sumikawa geothermal plant (Hachimantai volcanic region, northern Japan) from 235 to 194 and 7 mg/L after 24 h treatment with 1 g/10 mL of HT (0.41 mg/g) and CHT (2.28 mg/g), respectively with no significant effect of temperature in the range of 25–80 $^{\circ}$ C. Lower sorption capacity of 1.17 mg/g was reported by Ref. [26] for CHT in B removal from GW of Yangbajing plant (Tibet, China) with 113.7 mg B/L. Obtaining much higher sorption capacity (up

to 22.2 mg/g) in B removal from boric acid solution [26], suggested the considerable negative effects of anions such as HCO_3^- , SO_4^{2-} , Cl^- and F^- on B removal and their competitions with H_3BO_3 and $B(OH)_4^-$ for available sorption sites on CHT surface.

5.2. Membrane technologies

Membrane technologies have recently attracted significant attention due to increasing pressures on readily available freshwater supplies [107,108]. Furthermore, their enhanced economic feasibility and improved large-scale applications have deemed membrane technologies effective in industrial and domestic high throughput applications. Membrane processes can be categorized based on the driving force of the system which can be pressure, concentration, temperature or electrical potential gradient. Besides desalination, their applications include removal of heavy metals, organic pollutants, suspended solids, and other

 Table 2

 Summary of membrane-based processes for geothermal water treatment.

Membrane process	Membrane type	Geothermal water resources	Optimum operating conditions	Removal efficiency (%)	References
UF	Ceramic fine	Kızıldere/Denizli/Turkey	C _{i.B} : 22.2 mg/L, pH: 8.8, MPS:4 nm, P: 8 bar, T: 55 °C	≈25-30	[113]
RO	BW30FR-400	Bańska PGP-1/Poland	C _{i.B} : 9.76 mg/L, P: 15 bar, T: 22 °C, PR: %50, MT: of B400	67.8	[120]
	BW30HR-440i		HR		
	AG Membrane				
	B400 HR				
RO	SWHR	Balcova/Izmir/Turkey	C _{i,B} : 9.4 mg/L, P: 35 bar, MT: SWHR, pH: 11, T: 34 °C	96	[118]
	BW-30 (FILMTE				
	AG (GE Osmonic)				
EDI	Neosepta AMX	Izmir/Turkey	C _{i,B} : 5.9 mg/L, Layered bed configuration of EDI, Q _{feed} :1.0	93.2	[121]
	Neosepta CMX		L/h, V: 40 V, EC: 500 μS/cm, MT: Selemion AHT and CMD		
	Selemion AHT				
	Selemion CMD				
	Selemion AME				
	Selemion CME				
RO	ROBW30HR-440i	GT-1/Poland	C _{i,B} : 9.76 mg/L, P: 15 bar, T: 22 °C	72.0	[122]
EDI	CMX-AMX	Post-treatment of RO permeate	C _{i,B} : 5.36 mg/L, V: 20 V, Q _{permeate} : 1.08 L/h, MT: CMX-	93.7	[123]
	CMB-AMH	of GW from Izmir/Turkey	AMX, cell number of multi		
	CMS-AHA				
	CMI7000-AMI7001				
RO	AD-SWRO	Izmir/Turkey	C _{i,B} : 10.9 mg/L, MT: AD-SWRO, P: 30 bar, CFV: 0.33 m/s	92.1	[120]
	AG-BWRO				
	BW-30-BWRO				
	AK-BWRO				
RO	BW30	Izmir/Turkey	C _{i,B} : 10.9 mg/L, MT: BW30, P: 20 bar, pH: 10.5	>99	[119]
NF	UTC-70C				
	TFC HR				
	NF90				
	NP030				
	NF99 HF	- / 1 - 2 - 2 - 1 - 1			54.0.43
UF-RO	UFC M5 type of UF membrane	Bańska IG-1/Poland	$C_{i,B}$: 9.46 mg/L, P: 15 bar, T: 30 °C, pH: 7.2	98.3	[124]
	BW30HR-440i type of RO				
20	membrane	·	0 114 % P 101 W 105	0.4.5.05	F1.1.03
RO	BW30-2540	Izmir/Turkey	C _{i,B} : 11.4 mg/L, P: 12 bar, pH: 10.5	94.5–95	[119]
RO	FilmTecTMSW30-2540	Izmir/Turkey	C _{i,B} : 11.4 mg/L, MT: SW30-2540, P: 20 bar, pH: 7.0	84	[125]
D.O.	FilmTec™XUSSW30XHR-254	I	C . 11 A (L C C	40	[110]
RO	BW30-2540	Izmir/Turkey	C _{i,B} : 11.4 mg/L, membrane configuration of single, P: 15 bar	49	[119]
UF-RO	BW30HR-440i	GT-1/Poland		96	[196]
UF-RO	UFC M5	G1-1/Polatid	C _{i,B} : 9.45 mg/L, P: 1.0 MPa, pH: 10, PR:75%.	90	[126]
AGMD	ENM	a geothermal power plant in	C _{i.B} : 60.84 mg/L, MT: PTFE micro powder added ENM,	99.6	[127]
AGMD	EINIVI	Turkey	membrane area of 44.18 cm ²	99.0	[12/]
AGMD	PP	Maren/Aydın, Turkey	$C_{i,B}$: 60.84 mg/L, membrane area of 44.18 cm ² , MT: PP	99.8	[117]
	PTFE	Maren/Ayum, Turkey	0.20, T: 70 °C, Q _{feed} : 1.4 L/min, airgap width of 3 mm.	99.0	[11/]
	PVDF		0.20, 1. / 0 G, Qfeed. 1.7 L/ IIIII, all gap width of 3 IIIIII.		
RO and NF	XLE-BWRO	Izmir/Turkey	C _{i,B} : 12 mg/L, P: 11 bar, OT: 4 h	58.3	[14]
	CK-NF	izimi/ i urkcy	S1,5. 12 1118/ L, r. 11 Dai, O1. 4 11	61.7	[17]
	NF90			38	
RO and NF	BW30-RO,	Izmir/Turkey	C _{i.B} : 5.6 mg/L, P: 12 bar, OT: 4 h	40.7 44.1 49.9	[14]
ICO and IVI	TR-NE90-NF	izimi/ i urkcy	O _{I,B} , o.o mg/ L, 1. 12 bm, O1. 7 H	10.7 77.1 77.7	[17]
	TR-BE-BW				

Notes: $C_{i,B}$: Initial boron concentration, ZW: ZeeWeed, ENM: Electrospun nanofibrous membranes, MPS: Membrane pore size, P: Pressure, MT: Membrane type, T: Temperature, PR: Permeate recovery, C_{resin} : Resin, $Q_{permeate}$: Permeate flow rate concentration, Q_{feed} : Feed flow rate, V: Voltage, EC: Electrical conductivity, $C_{adsorbent}$: Adsorbend concentration, Q_{air} : Air flow rate, OT: Operating time, CFV: Cross flow velocity, RT: Resin type.

pollutants from saline or wastewater sources including GWs [109-112].

Membrane processes such as forward osmosis (FO), reverse osmosis (RO), ultrafiltration (UF), nanofiltration (NF), microfiltration (MF), membrane distillation (MD), and electro-deionization (EDI) have been thoroughly investigated for desalination of water streams with high ionic content. A focused literature summary on membrane processes for the B treatment in GW studies is listed in Table 2. The reported B removal rates from GW at their natural pH obtained by most tested membrane techniques in sole were generally inadequate except for air gap membrane distillation (AGMD) and seawater reverse osmosis (SWRO). This is explained by the dominancy of non-ionic H₃BO₃ at natural pH of GW (<9) which makes the size exclusion the main process of B removal in membrane techniques. The molecular size of boric acid (~155 nm) is generally smaller than the network pores of many commercialized membranes (\sim 0.100–0.300 nm). In addition, similar transport behaviours of H₃BO₃ and water molecules due to their similar hydrogen bonding adversely affect B treatment using membrane technologies [14,113].

RO is the most applied membrane technique for B treatment of GW. There are various commercially available RO systems used for B treatment in GWs which are classified into two main groups of brackish water (BWRO) and sea water reverse osmosis (SWRO). In general, higher removal efficiencies have been reported for SWRO. At the operation pressure (OP) of 15.5 bar [114], obtained the B removal efficiency range of 73-89% by SWRO compared to 60-85% by BWRO in treatment of GW of City of Izmir. Higher B removal by SWRO compared to BWRO was also reported by Ref. [115]. In their research, 84.5% B removal efficiency was obtained by AD-SWRO compared to 65.6% by BW-30 in the treatment of GW of Izmir Turkey with B concentration of 10.5-10.9 mg/L, at pH=8.6, and OP=15 bar. Increasing the OP to 30 bar led to the increase in the removal rate to 92% by AD-SWRO resulted in an effluent with 0.86 mg B/L which was deemed appropriate for irrigation. However, analyses of monovalent and divalent anion and cations suggested that mineralization would be required before usage in irrigation.

Among the membrane techniques, air gap membrane distillation (AGMD) has shown the highest B removal rate from GWs containing relatively high B concentration. AGMD is considered as one of the most versatile membrane techniques in which an air gap separates the hydrophobic membrane from a cool condensing surface [116]. [117] used AGMD process for B removal from GW resources in Aydın, Turkey. AGMD process performance was optimized for different operating variables such as membrane type, feed water temperature and velocity, and air gap distance. The maximum B removal efficiency of 99.8% was achieved in the treatment of GW with 60.84 mg B/L under the optimized condition (membrane surface area of 44.18 cm², membrane type of PP 0.20 μ M, feed temperature of 70 °C, feed flowrate of 1.4 L/min, and air gap width of 3 mm). In contrast, UF was suggested as the less effective membrane technologies for B treatment in GWs compared to other types such as RO and AGMD [113]. reported low B removal rates of 25-30% for ceramic fine UF in the treatment of GW of Kızıldere power plant in Denizli, Turkey (B = 22.2 mg/L, pH = 8.8). However, NF could give comparable removal rates to those obtained by RO at low OP depending on the type of tested NF and [14]. obtained a B removal rate of 61.7% in the treatment of GW of Izmir Energy Co. with 12 mg B/L by NF90 which was slightly higher than 58.3% obtained by XLE-BWRO at OP of 11 bar. However, they reported a removal rate of 38% for NF-CK which was much lower than both the other tested NF type and RO in their research. These researchers also compared performances of two BWRO with a NF membrane configuration in B treatment of a spent geothermal production well in Izmir Energy Co. with 5.6 mg B/L at OP of 12 bar through a pilot study. A removal rate of 44.1% was obtained by TR-NE90-NF after 4 h which was slightly higher than 40.7% obtained by BW30-RO, and slightly lower than 49.9% obtained by TR-BE-BW, respectively.

It has been discussed that optimizing the operational conditions such as initial B condition, permeate and feed flow rate and temperature, applied pressure, pH, etc. can enhance the membrane technology

performances. While no effect of initial B concentration on B removal by RO was reported for a low range of 9.4-24.8 mg B/L [118], pH has shown as the most effective parameter to be optimized as it leads to the dissociation of H₃BO₃ to B(OH)₄ which results in increasing the size of B-containing molecule by hydration (enhancing size exclusion) and charge repulsion by negatively charged membrane surface [119]. However, increasing pH could result in increasing cost, enhanced scale formation (reduces flux rate), and higher membrane degradation [119]. reported a significant increase (from 47 to 95%) in B removal efficiency using RO system of BW30-2450 treating GW of Izmir geothermal field with 11.4 mg B/L by increasing pH from 8.5 to 10.5 with the addition of NaOH which led to an effluent with 0.5 mg B/L suitable for irrigation. The significant increase in B removal by a membrane technique by increasing pH to 10.5 was also reported by Ref. [86] who obtained a B removal rate of >99% in treatment of GW of City of Izmir with B concentration of 10.2 mg/L and original pH of 8.1. Such high removal efficiency range (96-97%) was also reported by Ref. [118] who evaluated the performance of SWHR (a RO type membrane system) in B treatment in GWs of Kızıldere (Kütahya) and Balçova (İzmir) with 24.8 and 9.4 mg B/L, respectively but at the much higher OP of 35 bar and adjusted pH of

Increasing OP has been suggested as one of the most effective solutions to enhance B removal of various membrane technologies including RO and NF [14]. [114] reported an increase of B removal from 53 to 75% by increasing OP from 6.9 to 20.1 bar in a BWRO system used for the treatment of Izmir GW with 10.2 mg B/L and pH of 8.1. They also observed an enhancement in B removal from 75 to 85 to 92-97% in SWRO system by increasing OP from 15.1 to 48.3 bar. However, further OP increase from 20.1 to 31 decreased B removal to 58% since higher permeate flux and recovery likely led to a higher degree of concentration polarization, and membrane deterioration/compaction. Increasing OP from 15 to 30 bar [111], reported increases in B removal rates obtained by BW-30 and AD-SWRO in treatment of GW of Izmir (10.5-10.9 mg B/L and pH = 8.6) with the higher increase in SWRO in which B removal rate improved from 84.5 to 92%. On the other hand, it has been suggested that increasing OP results in increasing treatment costs and removing monovalent and divalent ions necessary for plants growth making additional mineralization necessary before reuse for irrigation [14,115].

5.3. Hybrid processes

As discussed in the previous section, the application of membrane technologies in sole to the B treatment in GWs may not be adequately effective. In addition, the suggested solutions in the literature such as increasing pH, OP for enhancement of effectiveness of membrane technologies can be associated with increasing costs and generating effluents inappropriate for irrigation purposes. Therefore, configuring hybrid operations that integrates a membrane process with another removal mechanism (usually adsorption) emerges as a viable solution. Hybrid processes have drawn significant interest due to their high removal efficiencies and applicability for high salinity streams that should be treated for specific goals. Several membrane-based hybrid processes were studied for B removal from GW resources (Table 3). The hybrid processes applying various membrane technologies and adsorbents (mostly resins) have been mostly effective in reducing B from about 10 mg/L to the values below 1 mg/L (with the removal efficiency range of 91.3-99.7% in most cases) recommended for irrigation although they have not been tested for GWs with higher B content. As discussed in Sections 5.1 and 5.2, limited successes were achieved using adsorption and membrane technologies in sole in reducing B in GWs to below 1 mg/L although a considerable number of studies on membrane technologies reported such that B removal efficiency with increasing pH and OP to high values which is associated with high cost and generating effluents needing further treatment to be used for irrigation.

It has been discussed in the literature that the particle size of commercially available resins (0.2–1 mm) restricts their usage in hybrid

Table 3Summary of studies on boron treatment in geothermal waters using membrane-based hybrid process.

Adsorbent type	Membrane type	Geothermal water resources	Optimum operating conditions	Removal efficiency (%)	References
Novel monodisperse nanoporous poly(GMA- co-EDM) and poly(VBC-co-DVB) resin beads	UF: ZW-1	Izmir/Turkey	C _{i,B} : 10.3 mg/L, C _{resin} : 3 g/L, Q _{permeate} : 10 mL/min, Q _{air} · 4 L/min	98.5	[129]
Dowex (XUS 43594.00)	BWRO: BW30-2540	Izmir/Turkey	C _{i,B} : 8.8 mg/L, P:15 bar for RO, pH: 8.0 for RO, C _{resin} : 1.5 g/L, Q _{permeate} : 10 mL/min	98.2	[103]
Dowex (XUS 43594.00)	UF: ZW-1	Izmir/Turkey	C _{i,B} : 9.37 mg/L, C _{adsorbent} : 1 g/L, Q _{permeate} :5.0 mL/min	83.1	[104]
Diaion CRB02 Dowex (XUS 43594.00)	MF: Hollow Fiber Membrane Module	Izmir/Turkey	C _{i,B} : 9.5 mg/L, Diaion CRB02: OT: 2 C _{resin} : 4.2 g/L Q _{permeate} : 0.5 mL/min Dowex (XUS 43594.00): OT:24 h C _{resin} : 2 g/L f 4.2 g/L Q _{permeate} : 1 mL/min	>99	[94]
Dowex (XUS 43594.00) Novel expanded gel-line VCB resin (2 JW)	UF: ZW-1	Izmir/Turkey	C _{i,B} : 9.95 mg/L, C _{resin} : 2 g/L, Q _{permeate} : 5 mL/min, OT: 180 min, pH: 8.4	(XUS 43594.00): 95 2JW: 91.7	[35]
Diaion CRB02 Dowex (XUS 43594.00)	MF: Hollow Fiber Membrane Module	Kizildere/Denizli/ Turkey,	C _{i,B} : 20 mg/L, OT: 20 min.	65–70%	[130]
Dowex (XUS 43594.00)	UF:ZW-1	Izmir/Turkey	C _{i,B} : 11.4 mg/L, C _{resin} : 2 g/L, OT: 20 min, Q _{permeate} : 20 mL/min	≈91.3	[103]

VBC: Vinylbenzylchloride, DVB: Divinylbenzene (DVB), GMA: Glycidyl methacrylate (GMA), EDM: Ethylene dimethacrylate, C_{i,B}: Initial boron concentration, ZW: ZeeWeed, MF: Microfiltration, ENM: Electrospun nanofibrous membranes, MPS: Membrane pore size, P: Pressure, MT: Membrane type, T: Temperature, PR: Permeate recovery, C_{resin}: Resin, Q_{permeate}: Permeate flow rate concentration, Q_{feed}: Feed flow rate, V: Voltage, EC: Electrical conductivity, C_{adsorbent}: Adsorbend concentration, Q_{air}: Air flow rate, OT: Operating time, CFV: Cross flow velocity, RT: Resin type.

systems. In the previous studies, commercially available BSRs have been grounded to an average particle size of 20 µm to be employed in a membrane-based hybrid process. However, grounding commercial BSRs may cause some heterogeneity and irregular shape in particles which may adversely affect the process sustainability [128]. Thus, the main challenge in the application of hybrid processes to the B treatment in GWs is obtaining a cost-effective adsorbent with a particle size that is small enough to prevent abrasion and cracking [35]. Therefore, novel sorbents with smaller sizes have been attracting more attention to maintain stability and reliability of hybrid processes [124]. For that purpose, it was indicated that the process of membrane emulsification followed by emulsion polymerization could give polymeric microspheres that provide effective fine adsorbents with high selectivity and sorption capacity [88]. Some recently developed novel resin beads functionalized with NMDG prepared using this method have shown comparable results with those of a grounded commercially available BSR, Dowex XUS-43594.00 in hybrid processes in which B reduced to below 1 mg/L from GWs with about 10 mg B/L but either with double resin's usage [128] or longer treatment time [35]. Although this suggests lower sorption capacities of novel resin beads, destroyed morphology of the grounded commercial BSRs encourage further research to improve sorption capacities of novel resin beads with smaller size as alternatives for commercial BSRs to be employed in hybrid processes.

5.4. Electrocoagulation

Electrocoagulation is one of the common methods of B treatment in water and wastewater. It uses a sacrificing anode usually aluminum (Al) and iron (Fe) to produce flocs for in-situ coagulation (see Fig. 8). The dissolution of Al/Fe parallel to water hydrolysis in anode, followed by generation of Al/Fe hydroxide flocs that subsequently generates larger flocs through aggregation process, and finally adsorption of H_3BO_3 and $B(OH)_4$ on the surface of the developed large flocs of the metal hydroxide is the mechanism of B removal from water in the electrocoagulation system. This mechanism can result in the simultaneous

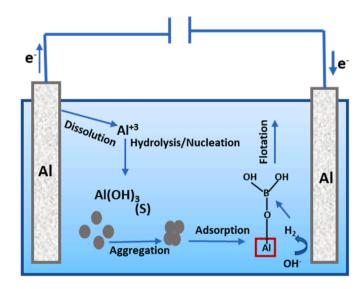


Fig. 8. Representative diagram of boron treatment using electrocoagulation [85,134].

removal of various contaminants from the water such as total suspended solids (TSS), phosphate, organic matters, As, F, and B via various routes, including adsorption, coprecipitation, charge neutralization, electroflotation, and sweep flocculation [131,132]. This advantage along with the reported optimal pH of 8 for B removal [37,133] using the electrochemical process suggest the process as a good candidate for B treatment in GW [84]. However, it has been discussed that the electrocoagulation may not be suitable for wastewaters with high B concentrations since the main mechanism is adsorption [84]. For instance Ref. [134], reported only 55% B removal using an electrocoagulation system treating mining wastewater with 500 mg/L. Nevertheless, it may be still an appropriate B treatment method for GWs with relatively lower B ranges such as Turkey [37]. obtained a high B removal rate of 95% in the treatment of

GWs of Ilica, Turkey with 24 mg B/L under pH of 8.0, electrolysis time of 30 min, current density of 6.0 mA/cm², and temperature of 60 $^{\circ}$ C. Despite providing the effluent with B less than 1 mg/L suitable for irrigation, no research other than [37] studied B treatment in GWs likely due to relatively high energy consumption and yielding lower rates at lower temperature (which usually is the case for the spent GW) and higher B concentration.

5.5. Challenges and future prospective in treatment

As discussed, the applications of various adsorbents, membrane technologies, hybrid processes, and electrocoagulation to the B treatment of GW have been subjects of different studies. With B adsorption on metal oxides (Al or Fe) flocs surfaces in situ generated by a sacrificing anode as the main treatment mechanism, electrocoagulation shows a promising perspective in B treatment of GWs with lower B ranges. However, it has not attracted interests of researchers likely due to high energy consumption. Therefore, adsorption, membrane technologies, and a combination of both have been of interest in recent research studies on B treatment of GW.

Among various adsorbents, resins, cellulose-based adsorbents, and metal oxides (or clay minerals containing metal oxides on their surfaces) have been studied for B treatment in GWs. One of the most important points to consider in B treatment using adsorbents is the presence of B in the non-ionized form of H₃BO₃ at pH < 9 (typical pH for GW) [84], which makes many common adsorbents relying on electrostatic sorption of metals with their negatively charged surface less effective. Reviewed studies clarify that BSRs and Chelest Fiber are the most common and effective adsorbent capturing B through the chelation process by their functional groups (NMDG as the most common ones). The good recovery and regeneration rates of these adsorbents [90] are also an advantage of these groups making them reusable in the treatment process along with recovering B to be used by other industries. While some drawbacks of BSRs such as hydrophobicity and poor structure of resin are addressed by Chelest Fiber, both are not recommended/tested for high B concentration (>100 mg/L) [83], making them less effective for GW treatment in some parts of the world where B concentration in GW is much higher such as Japan, China, and Mexico [26,56,97]. Despite their lower sorption capacity compared to BSRs and Chelest Fiber, metal oxides have shown effective candidates for GWs with high B content due to their low cost being available from waste (e.g., metal slags) [101] or naturally occurring clay minerals like HT with costs of calcination through thermal activation and chemical synthesis as low as 5.65 USD/kg [26]. However, their regeneration and B recovery rates, and ability to produce effluents with neutral pH and B lower than 1 mg/L useable for irrigation need further research.

Various membrane technologies have been used for B treatment in GWs. The performance of membrane technologies used in sole was generally low except for AGMD and SWRO as size exclusion is the main separation mechanism at the natural pH range of GW [14,113]. At the natural pH range of GWs, H₃BO₃ with the smaller molecule than many membranes' pore sizes is the dominant B species making B treatment by them less effective. Increasing pH to higher than 9.4 dissociates H₃BO₃ to B(OH)4 which leads to higher removal rates due to both larger size of B(OH)₄ caused by hydration and repulsion by the negatively charged membrane surfaces [119]. Increasing OP can also increase B removal rate in most cases but it removes the other cations necessary for plants' growth [115]. In addition, it has been reported that excessive OP increase led to decrease in B removal rates in BWRO system likely due to higher degree of concentration polarization, and membrane deterioration/compaction caused by higher permeate flux and recovery [114]. Increasing OP and pH also increase the treatment cost and make more evaluation of the effluents necessary to be used for irrigation as it generates effluents with low useful cations and high pH which both could be $\,$ against plant's growth. Although scaling enhances B removal rates of membrane technologies in short-term by narrowing membrane pores, it decreases the productivity of membranes by reducing flux rates in the membranes. Thus, antiscalants should be used to avoid salt precipitation which increase the operational costs associated by B treatment in GWs using membrane techniques [14].

The discussed challenges in B treatment of GWs using membrane technologies in sole emerged hybrid systems which employs membrane technologies with BSRs as a viable solution. Despite the successful B removal to values below 1 mg/L suitable for irrigation using hybrid process, large particle sizes of BSRs limit their application to B treatment of GWs. As grounding of BSRs negatively affect the sustainability of hybrid system caused by heterogeneity and irregular shape of particles, the new trend of research is on developing cost-effective adsorbents with smaller particle sizes to be employed in hybrid systems. In line with this trend, some recently developed novel beads with fine particles have shown similar B removal rates to those of grounded commercially available one (Dowex XUS-43594.00) in hybrid systems but either with longer treatment [35] or double resin usage [128] which encourages further research on increasing sorption capacity of these novel fine particle resin beads due to destroyed morphology of grounded commercial resins.

Developments on the techno-economic understanding and life cycle analysis of boron recovery by various methods are limited whilst the subject is critical for developing sustainable solutions [135]. presented a techno-economic assessment of the recovery of boric acid by honeycomb-like porous magnetic hybrids. The costs associated with the operational cost including the eluent used, chemicals, electrical energy and fixed costs associated with the recovery were considered for the treatment of 72 m³/year boron effluent over five year period of depreciation charges of equipment. Considering 75% recovery of Boron in the form of boric acid, they showed that the recovery by the hybrid system used is economically feasible. In the state-of-the-art-review on adsorption and coagulation techniques for the removal of boron from wastewater by Ref. [84]; economic considerations for adsorption based systems are qualitatively discussed. Aspects of regeneration are mentioned in relation to clay-based technologies [84] which can also be important in other methods. Life cycle analysis (LCA) studies on geothermal energy are emerging in literature (e.g. Ref. [136]) and they indicate the need for critical LCA analysis of the environmental impacts on the overall geothermal energy sector. Our study of the literature also highlights the absence of detailed life cycle analysis for B recovery for competitive methods for treatment.

6. Conclusions

One of the most important environmental challenges of GE production can be water contamination by boron. Despite the importance of the issue, there exists a knowledge gap in the sources, mechanism of release, ranges, speciation, and management (treatment and recovery) of B in GWs in all around the world and data in the literature on these subjects are clustered. This critical review comprehensively evaluated these topics in the literature and discusses challenges and future perspectives in boron treatment of GWs which are useful for environmental management teams enabling them to better manage water contamination caused by GE plants.

Boron contamination in geothermal sites could be due to flawed production/re-injection wells construction and uncontrolled GW discharge to surface waters. Re-injection of spent GWs and their treatment for reuse in agriculture are the main water pollution management methods. The selection of treatment process depends on boron concentration range and speciation, cost of the treatment, and environmental consideration. Boron concentration in GW originated either from magmatic intrusion or water-rock interaction or both could have an extensive range of less than 10 to over 500 mg/L depending on the geology setting of the region. However, B is usually found in the form of non-ionic H_3BO_3 at the natural pH of GW (\sim 8) regardless of the region. This makes the selection of the B treatment method for GWs limited to

sorption using chelation process by functional groups of NMDG and metal oxides, size exclusion by membrane processes, and combination of them in hybrid processes.

BSRs, some membrane technologies such as BWRO and SWRO under high OPs and elevated pH, and hybrid processes could decrease B to less than 1 mg/L suitable for irrigation in low-B containing GWs along with appropriate B recovery rates. However, several drawbacks in each treatment method along with the lack of knowledge in their performance for high-B containing GWs, make further research necessary. Limited surface area, hydrophobicity of the polystyrene, poor chemical and thermal stability, unordered pore structure, high cost of regeneration associated with BSRs encourage research to find environmentally friendly and cost-effective B adsorbents. As membrane technologies in sole could not effectively remove boron from GW, hybrid systems which use a combination of membrane technologies and BSRs have attracted increasing attentions. However, the large particle size of commercially available BSRs limit their application in hybrid systems. As grounding commercially available BSRs negatively affect the sustainability of hybrid systems caused by destroyed morphology of resin, recent research has focused on developing resins with fine particles. The performance of these methods for high-B containing GWs requires further research.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgement

The financial support provided for this study as part of the project GeoGrab funded jointly by the British Council (Project No. 119N310) and The Scientific and Technological Research Council of Turkey (TUBITAK) is gratefully acknowledged.

References

- Organisation for Economic Co-operation and Development. Energy technology perspectives 2016: towards sustainable urban energy systems. Paris, France: International Energy Agency; 2016.
- [2] Pan S-Y, Gao M, Shah KJ, Zheng J, Pei S-L, Chiang P-C. Establishment of enhanced geothermal energy utilization plans: barriers and strategies. Renew Energy 2019;132:19–32. https://doi.org/10.1016/j.renene.2018.07.126.
- [3] Finster M, Clark C, Schroeder J, Martino L. Geothermal produced fluids: characteristics, treatment technologies, and management options. Renew Sustain Energy Rev 2015;50:952–66. https://doi.org/10.1016/j.rser.2015.05.059.
- [4] Moya D, Paredes J, Kaparaju P. Technical, financial, economic and environmental pre-feasibility study of geothermal power plants by RETScreen – Ecuador's case study. Renew Sustain Energy Rev 2018;92:628–37. https://doi.org/10.1016/j. rser 2018 04 027
- [5] Soltani M, Moradi Kashkooli F, Souri M, Rafiei B, Jabarifar M, Gharali K, et al. Environmental, economic, and social impacts of geothermal energy systems. Renew Sustain Energy Rev 2021;140:110750. https://doi.org/10.1016/j. rser.2021.110750.
- [6] Sharifi R, Moore F, Keshavarzi B. Mobility and chemical fate of arsenic and antimony in water and sediments of Sarouq River catchment, Takab geothermal field, northwest Iran. J Environ Manag 2016;170:136–44. https://doi.org/ 10.1016/j.jenyman.2016.01.018.
- [7] González-Ácevedo ZI, García-Zarate MA, Núñez-Zarco EA, Anda-Martín BI. Heavy metal sources and anthropogenic enrichment in the environment around the Cerro Prieto Geothermal Field, Mexico. Geothermics 2018;72:170–81. https:// doi.org/10.1016/j.geothermics.2017.11.004.
- [8] Liu M, Guo Q, Luo L, He T. Environmental impacts of geothermal waters with extremely high boron concentrations: insight from a case study in Tibet, China. J Volcanol Geoth Res 2020;397:106887. https://doi.org/10.1016/j. ivolgeores.2020.106887.
- [9] Guo Q, Wang Y, Liu WB. As, and F contamination of river water due to wastewater discharge of the Yangbajing geothermal power plant, Tibet, China.

- Environ Geol 2008;56(1):197–205. https://doi.org/10.1007/s00254-007-1155-2
- [10] Guo Q, Wang Y, Liu W. Hydrogeochemistry and environmental impact of geothermal waters from Yangyi of Tibet, China. J Volcanol Geoth Res 2009;180 (1):9–20. https://doi.org/10.1016/j.jvolgeores.2008.11.034.
- [11] Available from: [https://www.wri.org/resources/charts-graphs/water-stress-countrly.
- [12] Bundschuh J, Tomaszewska B. Geothermal water management. first ed. Boca Raton: CRC Press; 2016.
- [13] Bundschuh J, Kaczmarczyk M, Ghaffour N, Tomaszewska B. State-of-the-art of renewable energy sources used in water desalination: present and future prospects. Desalination 2021;508:115035. https://doi.org/10.1016/j. desal.2021.115035.
- [14] Jarma YA, Karaoğlu A, Tekin Ö, Baba A, Ökten HE, Tomaszewska B, et al. Assessment of different nanofiltration and reverse osmosis membranes for simultaneous removal of arsenic and boron from spent geothermal water. J Hazard Mater 2021;405:124129. https://doi.org/10.1016/j. jhazmat.2020.124129.
- [15] İpekçi D, Altıok E, Bunani S, Yoshizuka K, Nishihama S, Arda M, et al. Effect of acid-base solutions used in acid-base compartments for simultaneous recovery of lithium and boron from aqueous solution using bipolar membrane electrodialysis (BMED). Desalination 2018;448:69–75. https://doi.org/10.1016/j. desal.2018.10.001.
- [16] Tut Haklidir FS, Haklidir M. Prediction of geothermal originated boron contamination by deep learning approach: at Western Anatolia Geothermal Systems in Turkey. Environ Earth Sci 2020;79(8). https://doi.org/10.1007/ s12665-020-08907-6.
- [17] Yokoyama T, Takahashi Y, Tarutani T. Simultaneous determination of arsenic and arsenious acids in geothermal water. Chem Geol 1993;103(1–4):103–11. https:// doi.org/10.1016/0009-2541(93)90294-S.
- [18] Ellis AJ, Mahon WAJ. Chemistry and geothermal systems. New York: Academic Press; 1977.
- [19] Kristmannsdóttir H, Ármannsson H. Environmental aspects of geothermal energy utilization. Geothermics 2003;32(4–6):451–61. https://doi.org/10.1016/S0375-6505(03)00052-X.
- [20] Aiuppa A, Avino R, Brusca L, Caliro S, Chiodini G, D'Alessandro W, et al. Mineral control of arsenic content in thermal waters from volcano-hosted hydrothermal systems: insights from island of Ischia and Phlegrean Fields (Campanian Volcanic Province, Italy). Chem Geol 2006;229(4):313–30. https://doi.org/10.1016/j. chemgeo.2005.11.004.
- [21] Baba A, Ármannsson H. Environmental impact of the utilization of geothermal areas. Energy Sources Part B 2006;1(3):267–78. https://doi.org/10.1080/ 15567240500397043
- [22] Available from: https://www.researchgate.net/publication/301680710_The Impacts_of_Geothermal_Fluid_Discharge_on_Surface_Water_Quality_with_ Emphasis on Arsenic.
- [23] Bundschuh J, Maity JP, Nath B, Baba A, Gunduz O, Kulp TR, et al. Naturally occurring arsenic in terrestrial geothermal systems of western Anatolia, Turkey: potential role in contamination of freshwater resources. J Hazard Mater 2013; 262:951–9. https://doi.org/10.1016/j.jhazmat.2013.01.039.
- [24] Birkle P, Merkel B. Environmental impact by spill of geothermal fluids at the geothermal field of Los Azufres, michoacán, Mexico. Water Air Soil Pollut 2000; 124(3/4):371–410. https://doi.org/10.1023/A:1005242824628.
- [25] Ramos Q, Armienta MA, Aguayo A, Cruz O. Evaluation of the interactions of arsenic (As), boron (B), and lead (Pb) from geothermal production wells with agricultural soils. Ecotoxicol Environ Saf 2021;211:111843. https://doi.org/ 10.1016/j.ecoenv.2020.111843.
- [26] Guo Q, Zhang Y, Cao Y, Wang Y, Yan W. Boron sorption from aqueous solution by hydrotalcite and its preliminary application in geothermal water deboronation. Environ Sci Pollut Res Int 2013;20(11):8210–9. https://doi.org/10.1007/s11356-013-1796-5.
- [27] Benelli, M., Benelli, M., Franci, T. The geothermal resource for power use in Italy: energy, environmental and social acceptance [in Italian)].
- [28] Aksoy N, Simşek C, Gunduz O. Groundwater contamination mechanism in a geothermal field: a case study of Balcova, Turkey. J Contam Hydrol 2009;103 (1–2):13–28. https://doi.org/10.1016/j.jconhyd.2008.08.006.
- [29] Rabet RS, Simsek C, Baba A, Murathan A. Blowout mechanism of Alasehir (Turkey) geothermal field and its effects on groundwater chemistry. Environ Earth Sci 2017;76(1). https://doi.org/10.1007/s12665-016-6334-6.
- [30] European Bank for Reconstruction and Development. Cumulative impact assessment of geothermal resources in Turkey: cumulative impact assessment report. 2020.
- [31] Landi M, Margaritopoulou T, Papadakis IE, Araniti F. Boron toxicity in higher plants: an update. Planta 2019;250(4):1011–32. https://doi.org/10.1007/ s00425-019-03220-4.
- [32] Uluisik I, Karakaya HC, Koc A. The importance of boron in biological systems. J Trace Elem Med Biol 2018;45:156–62. https://doi.org/10.1016/j. jtemb.2017.10.008.
- [33] Tanaka M, Fujiwara T. Physiological roles and transport mechanisms of boron: perspectives from plants. Pflügers Archiv 2008;456(4):671–7. https://doi.org/ 10.1007/s00424-007-0370-8.
- [34] Bundschuh J, Tomaszewska B, editors. Geothermal water management. CRC Press; 2018.
- [35] Çermikli E, Şen F, Altıok E, Wolska J, Cyganowski P, Kabay N, et al. Performances of novel chelating ion exchange resins for boron and arsenic removal from saline

- geothermal water using adsorption-membrane filtration hybrid process. Desalination 2020;491:114504. https://doi.org/10.1016/j.desal.2020.114504.
- [36] Moss SA, Napal NK. Ambient water quality guidelines for boron. 2003.
- [37] Yilmaz AE, Boncukcuoğlu R, Kocakerim MM, Yilmaz MT, Paluluoğlu C. Boron removal from geothermal waters by electrocoagulation. J Hazard Mater 2008;153 (1–2):146–51. https://doi.org/10.1016/j.jhazmat.2007.08.030.
- [38] Available from: https://www.who.int/publications/i/item/9789241549950.
- [39] Darwish NB, Kochkodan V, Hilal N. Boron removal from water with fractionized Amberlite IRA743 resin. Desalination 2015;370:1–6. https://doi.org/10.1016/j. desal.2015.05.009.
- [40] Textile industry wastewater discharge quality standards. Zero Discharge of Hazardous Chemicals; 2016.
- [41] Ministry of Health Malaysia. mal189903. 2004.
- [42] Environmental Public Health (Water suitable for drinking) (No. 2) regulations 2019 - Singapore statutes online. [February 13, 2022]; Available from: https://sso.agc.gov.sg/SL-Supp/S274-2019/Published/20190401190000? DocDate=20190401190000.
- [43] Allowable limits for trade effluent discharge to watercourse or controlled watercourse. National Environment Agency of Singapore.
- [44] Bureau of Indian Standards. IS 10500 (2012): Drinking water
- [45] Haklıdır FST, Şengün R. Hydrogeochemical similarities and differences between high temperature geothermal systems with similar geologic settings in the Büyük Menderes and Gediz Grabens of Turkey. Geothermics 2020;83:101717. https:// doi.org/10.1016/j.geothermics.2019.101717.
- [46] Standards for drinking water quality. 2006.
- [47] Integrated wastewater discharge standard. Shanghai Municipal Environmental Protection Bureau; 2018.
- [48] Integrated wastewater discharge standard (DB 21/1627-2008): Department of Ecology and Environmental of Liaoning Province; 2008; Available from: http:// sthj.ln.gov.cn/xxgk/bzygf/hjbzgl/zcfg/dfbzwb/201905/t20190505_3671884. html
- [49] Requisitos de calidad del agua para diferentes usos. 1978.
- [50] Yılmaz EE, Özgür N. Hydrogeological, hydrogeochemical and isotope geochemical features of geothermal waters in tekkehamam and environs, western Anatolia, Turkey. Procedia Earth Planet Sci 2017;17:177–80. https://doi.org/ 10.1016/j.proeps.2016.12.057.
- [51] Millot R, Hegan A, Négrel P. Geothermal waters from the Taupo volcanic zone, New Zealand: Li, B and Sr isotopes characterization. Appl Geochem 2012;27(3): 677–88. https://doi.org/10.1016/j.apgeochem.2011.12.015.
- [52] Battistel M, Hurwitz S, Evans WC, Barbieri M. The chemistry and isotopic composition of waters in the low-enthalpy geothermal system of Cimino-Vico Volcanic District, Italy. J Volcanol Geoth Res 2016;328:222–9. https://doi.org/ 10.1016/i.jvolgeores.2016.11.005.
- [53] Aggarwal JK, Palmer MR, Bullen TD, Arnórsson S, Ragnarsdóttir KV. The boron isotope systematics of Icelandic geothermal waters: 1. Meteoric water charged systems. Geochem Cosmochim Acta 2000;64(4):579–85. https://doi.org/ 10.1016/S0016-7037(99)00300-2.
- [54] Ü Gemici, Tarcan G. Distribution of boron in thermal waters of western Anatolia, Turkey, and examples of their environmental impacts. Environ Geol 2002;43 (1–2):87–98. https://doi.org/10.1007/s00254-002-0608-x.
- [55] Leeman WP, Tonarini S, Pennisi M, Ferrara G. Boron isotopic variations in fumarolic condensates and thermal waters from Vulcano Island, Italy: implications for evolution of volcanic fluids. Geochem Cosmochim Acta 2005;69 (1):143–63. https://doi.org/10.1016/i.gca.2004.04.004.
- [56] Bernard R, Taran Y, Pennisi M, Tello E, Ramirez A. Chloride and Boron behavior in fluids of Los Humeros geothermal field (Mexico): a model based on the existence of deep acid brine. Appl Geochem 2011;26(12):2064–73. https://doi. org/10.1016/i.apgeochem.2011.07.004.
- [57] Wu S-F, You C-F, Lin Y-P, Valsami-Jones E, Baltatzis E. New boron isotopic evidence for sedimentary and magmatic fluid influence in the shallow hydrothermal vent system of Milos Island (Aegean Sea, Greece). J Volcanol Geoth Res 2016;310:58–71. https://doi.org/10.1016/j.jvolgeores.2015.11.013.
- [58] Palmer MR. Boron isotope systematics of hydrothermal fluids and tourmalines: a synthesis. Chem Geol 1991;94(2):111–21. https://doi.org/10.1016/S0009-2541 (10)80023-3
- [59] Purnomo BJ, Pichler T. Geothermal systems on the island of Java, Indonesia. J Volcanol Geoth Res 2014;285:47–59. https://doi.org/10.1016/j. jvolgeores.2014.08.004.
- [60] Tong W, Liao Z, Liu S, Zhang Z, You M, Zhang M. Thermal springs in Tibet. Beijing: Science Press: 2000.
- [61] Alçiçek H, Bülbül A, Brogi A, Liotta D, Ruggieri G, Capezzuoli E, et al. Origin, evolution and geothermometry of the thermal waters in the Gölemezli geothermal field, Denizli basin (SW Anatolia, Turkey). J Volcanol Geoth Res 2018;349:1–30. https://doi.org/10.1016/j.jvolgeores.2017.07.021.
- [62] Balaban TÖ, Bülbül A, Tarcan G. Review of water and soil contamination in and around Salihli geothermal field (Manisa, Turkey). Arabian J Geosci 2017;10(23). https://doi.org/10.1007/s12517-017-3299-z.
- [63] Ozgur N, Tekkanat SZ. Geothermal waters in the area between guvendik and malgaçemir (Aydin), western Anatolia, Turkey. IOP Conf Ser Earth Environ Sci 2019;362(1):12006. https://doi.org/10.1088/1755-1315/362/1/012006.
- [64] Bozdağ A. Hydrogeochemical and isotopic characteristics of Kavak (Seydişehir-Konya) geothermal field, Turkey. J Afr Earth Sci 2016;121:72–83. https://doi.org/10.1016/j.jafrearsci.2016.05.019.
- [65] Liao Z, Zhao P. Yunnan-Tibet geothermal belt-geothermal resource and case histories. Beijing: Science Press; 1999.

- [66] Guo Q, Liu M, Li J, Zhang X, Wang Y. Acid hot springs discharged from the Rehai hydrothermal system of the Tengchong volcanic area (China): formed via magmatic fluid absorption or geothermal steam heating? Bull Volcanol 2014;76 (10). https://doi.org/10.1007/s00445-014-0868-9.
- [67] Giggenbach WF. Geothermal solute equilibria. Derivation of Na-K-Mg-Ca geoindicators. Geochem Cosmochim Acta 1988;52(12):2749–65. https://doi.org/ 10.1016/0016-7037(88)90143-3.
- [68] Pennisi M, Leeman W, Tonarini S, Pennisi A, Nabelek P. Boron, Sr, O, and H isotope geochemistry of groundwaters from Mt. Etna (Sicily)—hydrologic implications. Geochem Cosmochim Acta 2000;64(6):961–74. https://doi.org/10.1016/S0016-7037(99)00382-8.
- [69] Roine A. HSC chemistry. 2006. Available from: www.outotec.com
- [70] MORATA Diego, ARAVENA Diego, Alfredo LAHSEN, Mauricio MUĀ'OZ, Pablo VALDENEGRO, editors. Chile up-date: the first South American geothermal power plant after one century of exploration. Iceland: Reykjavik; 2021.
- [71] Giudetti G, Tempesti L. First geochemical data from cerro pabellón geothermal project (Apacheta region, Chile). 2021.
- [72] Tassi F, Aguilera F, Darrah T, Vaselli O, Capaccioni B, Poreda RJ, et al. Fluid geochemistry of hydrothermal systems in the Arica-Parinacota, Tarapacá and Antofagasta regions (northern Chile). J Volcanol Geoth Res 2010;192(1–2):1–15. https://doi.org/10.1016/j.jvolgeores.2010.02.006.
- [73] Sanchez-Alfaro P, Reich M, Arancibia G, Pérez-Flores P, Cembrano J, Driesner T, et al. Physical, chemical and mineralogical evolution of the Tolhuaca geothermal system, southern Andes, Chile: insights into the interplay between hydrothermal alteration and brittle deformation. J Volcanol Geoth Res 2016;324:88–104. https://doi.org/10.1016/j.jvolgeores.2016.05.009.
- [74] Wrage J, Tardani D, Reich M, Daniele L, Arancibia G, Cembrano J, et al. Geochemistry of thermal waters in the Southern Volcanic Zone, Chile – implications for structural controls on geothermal fluid composition. Chem Geol 2017;466:545–61. https://doi.org/10.1016/j.chemgeo.2017.07.004.
- [75] Tang YP, Chung TS, Weber M, Maletzko C. Development of novel diolfunctionalized silica particles toward fast and efficient boron removal. Ind Eng Chem Res 2017;56(40):11618–27. https://doi.org/10.1021/acs.iecr.7b03115.
- [76] Anderson JL, Eyring EM, Whittaker MP. Temperature jump rate studies of polyborate formation in aqueous boric acid 1. J Phys Chem 1964;68(5):1128–32. https://doi.org/10.1021/j100787a027.
- [77] Deng Y, Nordstrom DK, Blaine McCleskey R. Fluoride geochemistry of thermal waters in Yellowstone National Park: I. Aqueous fluoride speciation. Geochem Cosmochim Acta 2011;75(16):4476–89. https://doi.org/10.1016/j. gca.2011.05.028.
- [78] Belova TP, Parshin BE, Latkin AS, Yakovishina OA, Zernova LD. Kornilova TI, ratchina TI. Stanford, California. In: Proceedings, thirty-fourth workshop on geothermal reservoir engineering stanford university; February 9-11, 2009. SGP-TR-187.
- [79] Lenzi A, Paci M, Giudetti G, Gambini R. Tracing ancient carbon dioxide emission in the larderello area by means of historical boric acid production data. Energies 2021;14(14):4401. https://doi.org/10.3390/en14144101.
- [80] Allegrini G, Luccioli F, Trivella A. Industrial uses of geothermal fluids at Larderello. Geothermics 1992;21(5–6):623–30. https://doi.org/10.1016/0375-6505(92)90015-2.
- [81] Climo M, Mroczek E, Carey B, Hill A, Barton B. Mineral extraction from New Zealand's geothermal brines: where to next? Presented at the New Zealand Geothermal Workshop (NZGW) Taupo. New Zealand 2015. 8-20 November.
- [82] Belova TP. Experimental studies in the sorptive extraction of boron and lithium from thermal waters. J Volcanol Seismol 2017;11(2):136–42. https://doi.org/ 10.1134/S0742046317020026.
- [83] Wang B, Guo X, Bai P. Removal technology of boron dissolved in aqueous solutions – a review. Colloids Surf A Physicochem Eng Asp 2014;444:338–44. https://doi.org/10.1016/j.colsurfa.2013.12.049.
- [84] Lin J-Y, Mahasti NNN, Huang Y-H. Recent advances in adsorption and coagulation for boron removal from wastewater: a comprehensive review. J Hazard Mater 2021;407:124401. https://doi.org/10.1016/j. ihazmat.2020.124401.
- [85] Bu T, Chen F, He X, Yang Y, Wang W. Researching the complexing conditions of residual boron in produced water from oil & gas fields. Process Saf Environ Prot Process 2018;116:254–61. https://doi.org/10.1016/j.psep.2018.02.013.
- [86] Kabay N, Güler E, Bryjak M. Boron in seawater and methods for its separation a review. Desalination 2010;261(3):212–7. https://doi.org/10.1016/j. desal.2010.05.033.
- [87] Güler E, Kabay N, Yüksel M, Yavuz E, Yüksel Ü. A comparative study for boron removal from seawater by two types of polyamide thin film composite SWRO membranes. Desalination 2011;273(1):81–4. https://doi.org/10.1016/j. desal.2010.10.045.
- [88] Wolska J, Bryjak M. Methods for boron removal from aqueous solutions a review. Desalination 2013;310:18–24. https://doi.org/10.1016/j. desal.2012.08.003.
- [89] Experimental study of boron recovery from geothermal water on ion exchange. 2010.
- [90] Recepoğlu YK, Kabay N, Yılmaz-İpek İ, Arda M, Yüksel M, Yoshizuka K, et al. Deboronation of geothermal water using N-methyl-D-glucamine based chelating resins and a novel fiber adsorbent: batch and column studies. J Chem Technol Biotechnol 2017;92(7):1540–7. https://doi.org/10.1002/jctb.5234.
- [91] Koseoglu P, Yoshizuka K, Nishihama S, Yuksel U, Kabay N. Removal of boron and arsenic from geothermal water in Kyushu island, Japan, by using selective ion exchange resins. Solvent Extr Ion Exch 2011;29(3):440–57. https://doi.org/ 10.1080/07366299.2011.573448.

- [92] Yilmaz-Ipek I, Koseoglu P, Yuksel U, Yasar N, Yolseven G, Yuksel M, et al. Separation of boron from geothermal water using a boron selective macroporous weak base anion exchange resin. Separ Sci Technol 2010;45(6):809–13. https://doi.org/10.1080/01496391003607357.
- [93] Hussain A, Sharma R, Minier-Matar J, Hirani Z, Adham S. Application of emerging ion exchange resin for boron removal from saline groundwater. J Water Proc Eng 2019;32:100906. https://doi.org/10.1016/j.jwpe.2019.100906.
- [94] Kabay N, Yilmaz-Ipek I, Soroko I, Makowski M, Kirmizisakal O, Yag S, et al. Removal of boron from Balcova geothermal water by ion exchange-microfiltration hybrid process. Desalination 2009;241(1-3):167-73. https://doi.org/10.1016/j.desal.2007.10.100.
- [95] Badruk M, Kabay N, Demircioglu M, Mordogan H, Ipekoglu U. Removal of boron from wastewater of geothermal power plant by selective ion-exchange resins. I. Batch sorption—elution studies. Separ Sci Technol 1999;34(13):2553–69. https://doi.org/10.1091/SCI.1001.0700
- [96] Kabay N, Yilmaz I, Yamac S, Samatya S, Yuksel M, Yuksel U, et al. Removal and recovery of boron from geothermal wastewater by selective ion exchange resins. I. Laboratory tests. React Funct Polym 2004;60:163–70. https://doi.org/ 10.1016/j.reactfunctpolym.2004.02.020
- [97] Wajima T. Removal of boron from geothermal water using hydrotalcite. Toxicol Environ Chem 2010;92(5):879–84. https://doi.org/10.1080/ 02772240903173312.
- [98] Samatya S, Tuncel A, Kabay N. Boron removal from geothermal water by a novel monodisperse porous poly(GMA- co -EDM) resin containing N -Methyl-D-Glucamine functional group. Solvent Extr Ion Exch 2012;30(4):341–9. https:// doi.org/10.1080/07366299.2012.686857.
- [99] Santander P, Rivas BL, Urbano BF, Yılmaz İpek İ, Özkula G, Arda M, et al. Removal of boron from geothermal water by a novel boron selective resin. Desalination 2013;310:102–8. https://doi.org/10.1016/j.desal.2012.08.026.
- [100] Kalaitzidou K, Tzika AM, Simeonidis K, Mitrakas M. Evaluation of boron uptake by anion exchange resins in tap and geothermal water matrix. Mater Today Proc 2018;5(14):27599–606. https://doi.org/10.1016/j.matpr.2018.09.080.
- [101] Belova TP, Ershova LS. Boron concentration by industrial anion exchanger resins from model solutions in a dynamic mode. Heliyon 2021;7(2):e06141. https://doi. org/10.1016/j.heliyon.2021.e06141.
- [102] Nishihama S, Sumiyoshi Y, Ookubo T, Yoshizuka K. Adsorption of boron using glucamine-based chelate adsorbents. Desalination 2013;310:81–6. https://doi. org/10.1016/j.desal.2012.06.021.
- [103] Kabay N, Köseoğlu P, Yavuz E, Yüksel Ü, Yüksel M. An innovative integrated system for boron removal from geothermal water using RO process and ion exchange-ultrafiltration hybrid method. Desalination 2013;316:1–7. https://doi. org/10.1016/j.desal.2013.01.020.
- [104] Recepoğlu YK, Kabay N, Ipek IY, Arda M, Yüksel M, Yoshizuka K, et al. Packed bed column dynamic study for boron removal from geothermal brine by a chelating fiber and breakthrough curve analysis by using mathematical models. Desalination 2018;437:1–6. https://doi.org/10.1016/j.desal.2018.02.022.
- [105] Mercado-Borrayo BM, Solís-López M, Schouwenaars Ř, Ramírez-Zamora RM. Application of metallurgical slag to treat geothermal wastewater with high concentrations of arsenic and boron. Int J Environ Sci Technol 2019;16(5): 2373–84. https://doi.org/10.1007/s13762-018-1952-z.
- [106] Peak D, Luther GW, Sparks DL. ATR-FTIR spectroscopic studies of boric acid adsorption on hydrous ferric oxide. Geochem Cosmochim Acta 2003;67(14): 2551-60. https://doi.org/10.1016/S0016-7037(03)00096-6.
- [107] Al-Najar B, Peters CD, Albuflasa H, Hankins NP. Pressure and osmotically driven membrane processes: a review of the benefits and production of nano-enhanced membranes for desalination. Desalination 2020;479:114323. https://doi.org/ 10.1016/j.desal.2020.114323.
- [108] Lee WJ, Ng ZC, Hubadillah SK, Goh PS, Lau WJ, Othman M, et al. Fouling mitigation in forward osmosis and membrane distillation for desalination. Desalination 2020;480:114338. https://doi.org/10.1016/j.desal.2020.114338.
- [109] Dorji P, Kim DI, Hong S, Phuntsho S, Shon HK. Pilot-scale membrane capacitive deionisation for effective bromide removal and high water recovery in seawater desalination. Desalination 2020;479:114309. https://doi.org/10.1016/j. desal_2020_114309
- [110] Li C, Feng G, Pan Z, Song C, Fan X, Tao P, et al. High-performance electrocatalytic microfiltration CuO/Carbon membrane by facile dynamic electrodeposition for small-sized organic pollutants removal. J Membr Sci 2020;601:117913. https:// doi.org/10.1016/j.memsci.2020.117913.
- [111] Park W, Jeong S, Im S-J, Jang am. High turbidity water treatment by ceramic microfiltration membrane: fouling identification and process optimization. Environ Technol Innovat 2020;17:100578. https://doi.org/10.1016/j. eti.2019.100578.
- [112] Zou Q, Zhang Z, Li H, Pei W, Ding M, Xie Z, et al. Synergistic removal of organic pollutant and metal ions in photocatalysis-membrane distillation system. ApplCatal B 2020;264:118463. https://doi.org/10.1016/j.apcatb.2019.118463.
- [113] Shultz S, Bass M, Semiat R, Freger V. Modification of polyamide membranes by hydrophobic molecular plugs for improved boron rejection. J Membr Sci 2018; 546:165–72. https://doi.org/10.1016/j.memsci.2017.10.003.
- [114] Koseoglu H, Harman BI, Yigit NO, Guler E, Kabay N, Kitis M. The effects of operating conditions on boron removal from geothermal waters by membrane

- processes. Desalination 2010;258(1–3):72–8. https://doi.org/10.1016/j.desal.2010.03.043.
- [115] Öner ŞG, Kabay N, Güler E, Kitiş M, Yüksel M. A comparative study for the removal of boron and silica from geothermal water by cross-flow flat sheet reverse osmosis method. Desalination 2011;283:10–5. https://doi.org/10.1016/j. desal.2011.02.038.
- [116] Alsebaeai MK, Ahmad AL. Membrane distillation: progress in the improvement of dedicated membranes for enhanced hydrophobicity and desalination performance. J Ind Eng Chem 2020;86:13–34. https://doi.org/10.1016/j. ijec.2020.03.006.
- [117] Ozbey-Unal B, Imer DY, Keskinler B, Koyuncu I. Boron removal from geothermal water by air gap membrane distillation. Desalination 2018;433:141–50. https:// doi.org/10.1016/j.desal.2018.01.033.
- [118] Cengeloglu Y, Arslan G, Tor A, Kocak I, Dursun N. Removal of boron from water by using reverse osmosis. Separ Purif Technol 2008;64(2):141–6. https://doi.org/ 10.1016/j.seppur.2008.09.006.
- [119] Yavuz E, Güler E, Sert G, Arar Ö, Yüksel M, Yüksel Ü, et al. Removal of boron from geothermal water by RO system-I—effect of membrane configuration and applied pressure. Desalination 2013;310:130–4. https://doi.org/10.1016/j. desal.2012.07.026
- [120] Tomaszewska B, Bodzek M, Rajca M, Tyszer M. Geothermal water treatment. Membrane selection for the RO process. Arch Environ Protect 2017;64:292–7. https://doi.org/10.5004/dwt.2017.11399.
- [121] Arar Ö, Yüksel Ü, Kabay N, Yüksel M. Application of electrodeionization (EDI) for removal of boron and silica from reverse osmosis (RO) permeate of geothermal water. Desalination 2013;310:25–33. https://doi.org/10.1016/j. desal.2012.10.001.
- [122] Tyszer M, Tomaszewska B. Pilot study of the impact of geothermal water RO concentrate volume minimization on the possibility of comprehensive further use. Desalination Water Treat 2019;157:250–8. https://doi.org/10.5004/dwt.2019.23910.
- [123] Bunani S, Arda M, Kabay N. Effect of operational conditions on post-treatment of RO permeate of geothermal water by using electrodeionization (EDI) method. Desalination 2018;431:100–5. https://doi.org/10.1016/j.desal.2017.10.032.
- [124] Tomaszewska B. The use of ultrafiltration and reverse osmosis in the desalination of low mineralized geothermal waters. Arch Environ Protect 2011;37(3):63–77.
- [125] Yavuz E, Arar Ö, Yüksel M, Yüksel Ü, Kabay N. Removal of boron from geothermal water by RO system-II-effect of pH. Desalination 2013;310:135–9. https://doi.org/10.1016/j.desal.2012.07.044.
- [126] Tomaszewska B, Bodzek M. Desalination of geothermal waters using a hybrid UF-RO process. Part II: membrane scaling after pilot-scale tests. Desalination 2013; 319:107–14. https://doi.org/10.1016/j.desal.2013.01.030.
- [127] Ozbey-Unal B, Gezmis-Yavuz E, Eryildiz B, Koseoglu-Imer DY, Keskinler B, Koyuncu I. Boron removal from geothermal water by nanofiber-based membrane distillation membranes with significantly improved surface hydrophobicity. J Environ Chem Eng 2020;8(5):104113. https://doi.org/10.1016/j. iecc.2020.104113.
- [128] Samatya S, Köseoğlu P, Kabay N, Tuncel A, Yüksel M. Utilization of geothermal water as irrigation water after boron removal by monodisperse nanoporous polymers containing NMDG in sorption–ultrafiltration hybrid process.

 Desalination 2015;364:62–7. https://doi.org/10.1016/j.desal.2015.02.030.
- [129] Kabay N, Ipek IY, Yilmaz PK, Samatya S, Bryjak M, Yoshizuka K, et al. Removal of boron and arsenic from geothermal water by ion-exchange. In: Bundschuh J, Tomaszewska B, editors. Geothermal water management. CRC Press; 2018. p. 135–55.
- [130] Yilmaz İ, Kabay N, Brjyak M, Yüksel M, Wolska J, Koltuniewicz A. A submerged membrane-ion-exchange hybrid process for boron removal. Desalination 2006; 198(1–3):310–5. https://doi.org/10.1016/j.desal.2006.01.031.
- [131] Garcia-Segura S, Eiband MMS, Melo JV de, Martínez-Huitle CA. Electrocoagulation and advanced electrocoagulation processes: a general review about the fundamentals, emerging applications and its association with other technologies. J Electroanal Chem 2017;801:267–99. https://doi.org/10.1016/j. jelechem.2017.07.047.
- [132] Lin J-Y, Raharjo A, Hsu L-H, Shih Y-J, Huang Y-H. Electrocoagulation of tetrafluoroborate (BF4-) and the derived boron and fluorine using aluminum electrodes. Water Res 2019;155:362–71. https://doi.org/10.1016/j. watres.2019.02.037.
- [133] Kartikaningsih D, Huang Y-H, Shih Y-J. Electro-oxidation and characterization of nickel foam electrode for removing boron. Chemosphere 2017;166:184–91. https://doi.org/10.1016/j.chemosphere.2016.09.091.
- [134] Güven ED, Güler E, Akıncı G, Bölükbaş A. Influencing factors in the removal of high concentrations of boron by electrocoagulation. J. Hazard. Toxic Radioact. Waste 2018;22(2):4017031. https://doi.org/10.1061/(ASCE)HZ.2153-5515.0000389.
- [135] Oladipo AA, Gazi M. Efficient boron abstraction using honeycomb-like porous magnetic hybrids: assessment of techno-economic recovery of boric acid. J Environ Manag 2016;183(3):917–24.
- [136] Tomasini-Montenegro C, Santoyo-Castelazo E, Gujba H, Romero RJ, Santoyo E. Life cycle assessment of geothermal power generation technologies: an updated review. Appl Therm Eng 2017;114:1119–36.