



Removal of boron from geothermal water by a novel boron selective resin

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HIGHLIGHTS

- ▶ A new chelating resin poly(*N*-(4-vinylbenzyl)-*N*-methyl-*D*-glucamine) for boron removal
- ▶ Removal of boron from geothermal water efficiently
- ▶ Higher capacity than that of commercial resin for boron removal
- ▶ Better kinetic performance than that of commercial resin for boron removal
- ▶ Better column utilization than that of commercial resin for boron removal.

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ABSTRACT

In this study, a novel chelating resin poly(*N*-(4-vinylbenzyl)-*N*-methyl-*D*-glucamine) (P(VbNMDG)) was synthesized. The sorption performance of this resin was compared with boron selective commercial resin Diaion CRB02 containing *N*-methyl-*D*-glucamine (NMDG) groups for boron removal from geothermal water. The P(VbNMDG) resin gave a higher sorption capacity and faster kinetics than that of Diaion CRB02 for boron removal from geothermal water. The kinetic data obtained were evaluated using classical kinetic models and diffusion/reaction models. It was concluded that both P(VbNMDG) and Diaion CRB02 resins obeyed pseudo second order kinetic model. Also, the rate controlling step of boron sorption was particle diffusion for both resins. The breakthrough profile of P(VbNMDG) resin for boron was sharper than that of Diaion CRB02. Thus, the degree of the column utilization of P(VbNMDG) resin was also high. The boron loaded on both resins was eluted using 5% H₂SO₄ solution with a percentage of around 80%.

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1. Introduction

In geothermal systems, the heated water circulates back to the surface through the host rock and as geothermal water ascends to the surface, it reacts with the wall rocks causing mineral dissolution [1]. Mineral–fluid equilibria play a fundamental role in determining the chemistry of the discharge fluids. The reactions which take place are a function of the temperature, pressure, salinity and host rocks of the geothermal system [2]. In geothermal waters, solute concentrations vary greatly and these differences are due to variations in temperature, gas content, heat source, rock type, permeability, age of the hydrothermal system and fluid source or mixing (for example with sea water).

Contamination of surface and subsurface waters with toxic heavy metals is the most severe environmental impact of geothermal energy. These contamination problems are mainly attributed to flawed well construction, faulty re-injection applications and uncontrolled discharge of

waste geothermal fluids to surface waters. As a consequence, surface and subsurface waters become chemically and thermally polluted [3]. Geothermal waters contain various kinds of species including boron and arsenic. The other ionic and nonionic species such as Cl[−], HCO₃[−], SO₄^{2−}, F[−], Br[−], I[−], Na⁺, K⁺, Li⁺, Ca²⁺, Mg²⁺, Rb⁺, Cs⁺, Mn²⁺, Fe²⁺, SiO₂, etc. can also exist. Gasses such as CO₂, H₂S, NH₃, N₂, H₂, and CH₄ are generally found in geothermal steams and are invariably present in geothermal discharges from both neutral features and wells [2].

Geothermal waters are generally used as irrigation water for agricultural areas. Their boron contents accumulate in the soil and this may cause a change in its characteristics. Also, these waters could mix with underground waters by passing through the soil and constitute complexes with Pb, Cu, Cd and Ni ions. The toxicities of these complexes are higher than those of the heavy metals alone [4]. Removal of boron from geothermal water is an important concern because of the reasons discussed previously.

Concentration of boron in groundwater throughout the world range is widely from <0.3 to > 100 mg/L [5]. Average surface water concentration of boron is about 0.1 mg/L but concentrations vary greatly,

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depending on boron content of local geologic formations and anthropogenic sources of boron. The presence of appreciable quantities of boron, both in drinking water and irrigation water deteriorates the quality of water. Therefore, WHO recommended in its guides for the quality of drinking water, a value with a maximum of 0.5 mg/L based on the NOEL (no-observed-adverse-effect-level) for many years. Recently, the WHO revised the Boron Guideline Value for drinking water at 2.4 mg/L [6]. On the other hand, if boron concentration in irrigation water is only slightly higher than the minimum, this will give a negative effect on plant growth and will present signs of boron toxicity. The tendency of boron to accumulate in vegetable tissues constitutes a potential hazard to the health of those consuming food and water with high boron content. As a result, although boron is vital as a micronutrient element for growth of plants, it can be detrimental at higher concentrations. Therefore, it is necessary to remove the excess amount of boron from water in an economical and feasible way. On the other hand, there is no easy method for removal of boron from water.

Simonnat et al. [7] have reviewed the methods of boron removal from drinking water. Recently, Yoshizuka et al. published a review on elimination of arsenic and boron from geothermal water [8]. The use of boron selective chelating ion exchange resins was considered to be still the most efficient method for boron removal [9–23].

Commercially available boron selective chelating ion exchange resins are generally prepared from macroporous poly(styrene-co-divinylbenzene) by functionalization with NMDG. The NMDG groups bind boron through a covalent attachment and an internal coordination complex formation [22]. Badruk et al. [12,13] used commercially available boron selective chelating resins Diaion CRB02 and Purolite S108 for boron removal from wastewaters of geothermal power plant. A mini pilot column-mode operation was performed in a geothermal field for the removal of boron from geothermal water containing boron at a concentration of 20 mg/L, running ten sorption-washing-elution-washing-regeneration-washing cycles [15]. Also, column performances of various NMDG type resins (Purolite S108, Diaion CRB01, Diaion CRB 02) and for boron removal from geothermal water were published before [14].

Recently, the synthesis of novel boron selective resins with high capacity, high selectivity, and high sorption rate received great interest for removal of boron from geothermal waters, seawaters, and reverse osmosis permeates. Wolska et al. prepared boron selective small particles (25 μm) reacting NMDG with poly(styrene-vinyl benzyl chloride-divinylbenzene). The resulted chelating resins showed a good performance in adsorption-membrane filtration hybrid system for removal of boron from water [24,25]. Samatya et al. reported on boron removal performances of monodisperse porous particles with dextrane based molecular brushes attached to the particles via “click chemistry” and “direct coupling”. They implied that these particles were efficient in boron removal from aqueous solution [26]. Elsewhere, monodisperse porous poly(glycidyl methacrylate-co-ethylene methacrylate) particles carrying diol functionality were reported to have a potential as boron selective resins [27]. These resins were used for removal of boron from geothermal water and its reverse osmosis permeates also [28]. Samatya et al. also produced a new sorbent with a high boron sorption capacity, using monodisperse porous poly(vinylbenzyl chloride-co-divinylbenzene) beads with a 8.5 μm in size which are synthesized by a new “modified seeded polymerization” technique. By using their chloromethyl functionality, the beads were derivatized by a simple and direct reaction with a boron selective ligand NMDG [29].

In this paper, we compared the boron sorption performances of two chelating resins bearing NMDG groups, considering their well-known selective properties for boron removal from water. One of the chelating resin is produced by polymerization of *N*-(4-vinylbenzyl)-*N*-methyl-D-glucamine (VbNMDG) monomer unit in presence of *N,N*-methylenebis-acrylamide (MBA) as the crosslinking agent. This resin had been studied previously for arsenic removal and it showed a high sorption capacity and fast kinetics for arsenic removal [30]. The other one is a

commercially available boron selective resin Diaion CRB02 prepared from hydrophobic poly(styrene-co-divinylbenzene) matrix.

2. Experimental

2.1. Materials

The monomer VbNMDG was synthesized from 4-vinylbenzylchloride (VBC, Aldrich) and NMDG (Aldrich). The reactants were used as received. The reagent MBA (98%, Aldrich) and ammonium persulfate (Aldrich) were used as crosslinker and initiator, respectively.

The chelating resin Diaion CRB02 was kindly supplied by Mitsubishi Chemical Co., Japan.

Geothermal water samples used in the experiments were taken from the geothermal heating center in Izmir City, Turkey. The chemical composition of geothermal water is shown in Table 1.

2.2. Preparation of chelating resin

2.2.1. Synthesis of VbNMDG monomer

In a three necked round bottom flask, the reaction of NMDG and VBC was carried out in a mole ratio of 1:1. The reagent grade NMDG (21.9 mmol) was dissolved in a solvent mixture of dioxane and deionized water (volume ratio of 2:1). The solution was added to the reactor and heated for 20 min until NMDG was completely dissolved. Next, 3.20 mL (21.9 mmol) of VBC was dissolved in 10 mL of dioxane and slowly added to the reactor. The reaction was kept under reflux with constant stirring for 5 h. To remove unreacted VBC, the solution was washed with ethyl ether twice.

2.2.2. Synthesis of P(VbNMDG)

In order to synthesize the chelating resin P(VbNMDG), the solution of VbNMDG monomer was subjected to polymerization via radical initiation. In the reaction flask, the crosslinker MBA (4 mol% with respect to the monomer) and the initiator ammonium persulfate (2 mol%) were added, and the mixture was degassed with nitrogen for 10 min. The reaction was stirred for 4 h under a nitrogen atmosphere at 75 °C. Then, the resin was extracted and washed with dioxane, distilled water, and dried in an oven at 50 °C. The synthesis route of P(VbNMDG) and the structure of Diaion CRB 02 were given in Fig. 1.

Table 1
Chemical composition of geothermal water.

Cations	Concentration (mg/L)	Anions	Concentration (mg/L)
Na ⁺ ^a	366	Cl ⁻ ^b	188
K ⁺ ^a	26.3	SO ₄ ²⁻ ^b	109
Ca ²⁺ ^a	26.2	F ⁻ ^c	4.45
Mg ²⁺ ^a	3.70	HCO ₃ ⁻ ^d	622
pH			8.6
EC ($\mu\text{S}/\text{cm}$)			1770
TDS (mg/L)			885
Salinity (‰)			0.7
Turbidity (NTU)			0.15
Si (mg/L)			56–65 ^e
B (mg/L)			10.5–10.9 ^f 10.25–11.00 ^g

^a AAS.

^b IC.

^c IS.

^d Titrimetric.

^e Colorimetric.

^f Spectrophotometric Curcumine method.

^g Azomethine method.

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