



Utilization of geothermal water as irrigation water after boron removal by monodisperse nanoporous polymers containing NMDG in sorption–ultrafiltration hybrid process



Saba Samatya ^{a,1}, Pelin Köseoğlu ^{b,2}, Nalan Kabay ^{b,*}, Ali Tuncel ^{a,*}, Mithat Yüksel ^b

^a Hacettepe University, Chemical Engineering Department, 35100 Izmir, Turkey

^b Ege University, Chemical Engineering Department, 35100 Izmir, Turkey

HIGHLIGHTS

- Application of novel polymer resins in sorption–ultrafiltration hybrid process.
- Boron removal from geothermal water by monodisperse nanoporous resin beads.
- Monodisperse porous chelating resins exhibited a good performance for boron sorption.
- Product water agreed well with irrigation water standards for boron.

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ABSTRACT

A relatively new method of polymerization, ‘modified seeded polymerization’ has been used for the synthesis of monodisperse nanoporous poly(glycidyl methacrylate-co-ethylene dimethacrylate) and poly(vinylbenzyl chloride-co-divinylbenzene) beads. The synthesized polymer beads were then functionalized with N-methyl-D-glucamine (NMDG) to obtain boron selective resins. The efficiency of these particles for boron removal from geothermal water was investigated by using the hybrid process coupling sorption with ultrafiltration (UF) method where a submerged hollow fiber type UF membrane module was employed for filtration. It was possible to reduce the boron concentration from 11.0 mg/L to ≤ 1 mg/L in 20 min with hybrid method using poly(glycidyl methacrylate-co-ethylene dimethacrylate)-NMDG beads with 4 g-resin/L-geothermal water. The respective period for poly(vinylbenzyl chloride-co-divinylbenzene) beads with the same resin dosage was 30 min. In the case of commercially available boron selective ion exchange resin Dowex-XUS 43594.00 ground to an average particle size of 20 μm , the target boron concentration which is ≤ 1 mg/L was reached in 20 min by using 2 g-resin/L-geothermal water.

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1. Introduction

Boron is an essential micronutrient element for plants. On the other hand, excess levels of boron in irrigation water could have harmful effect for some plants [1,2]. For many years, the permissible concentration of boron was 0.5 mg/L in drinking water by the World Health Organization (WHO), but this value was revised in 2011 and modified as 2.4 mg/L due to the positive effects of boron for human health [3].

However, some utilities may still set desalination plants product water limits lower than 1 mg/L, bearing the agricultural-related issues in mind.

Geothermal waters may contaminate the irrigation water in agricultural regions. Their boron accumulates in the soil and this may cause a change in the characteristics of it. Another risk is that the geothermal waters could mix with underground waters and form complexes with some heavy metal ions. The toxicities of these boron–metal complexes are mentioned to be more serious than those of the heavy metals alone. The high levels of boron may cause some serious damages on some plants having low boron tolerance [4,5]. Various technologies have been suggested in the published literature to reduce boron concentration in water and wastewater. The main processes are adsorption, ion exchange and membrane processes [6–11].

The hybrid process combining sorption and membrane filtration is recently introduced as an effective method for water treatment. It

* Corresponding authors.

E-mail addresses: nalan.kabay@ege.edu.tr (N. Kabay), atuncel@hacettepe.edu.tr (A. Tuncel).

¹ Present address: Siirt University, Chemical Engineering Department, Siirt, Turkey.

² Present address: Istanbul University, Faculty of Pharmaceutical Sciences, Istanbul, Turkey.

Table 1
Chemical composition of geothermal water.

Cations	Concentration (mg/L)	Anions	Concentration (mg/L)
Na ⁺	366	Cl ⁻	188
K ⁺	26.3	SO ₄ ²⁻	109
Ca ²⁺	26.2	F ⁻	4.50
Mg ²⁺	3.70	HCO ₃ ⁻	622
pH	8.6		
EC (μS/cm)		1770	
TDS (mg/L)		885	
Salinity (‰)		0.7	
Turbidity (NTU)		0.15	
B (mg/L)		10.3–11.0	

allows removing and/or to recovering some species that can exist in water even at trace amounts [12]. In the first step of the hybrid process, the target component is bound to the coupling agent and, as a large complex, it is retained by the membrane. The complex is decomposed in the second step by using a suitable stripping solution followed by the membrane separation that recycles the binding agent. The recent developments in the materials science introduced novel sorbents and binding agents such as organic and inorganic sorbents, chelating and ion exchange resins, molecularly imprinted polymers and coordinating agents, micelles and colloids. They can be employed in the hybrid processes intensively when their sizes are small enough such as from few nanometers to dozens of micrometers. Recently, an extensive book chapter about hybrid processes and some case studies on the application of some inorganic or organic materials in such hybrid processes for environmental clean-up was published [12].

The chelating ion exchange resins have slow kinetics due to the diffusion-controlled rate limiting processes although they have a high selectivity. Poor kinetics is one of the major limitations for utilizing chelating ion exchange resins in water treatment applications [13]. In ion exchange operations, particle diameter in a packed bed influences pressure drop and kinetics of ion exchange [14]. The pressure drop is inversely proportional to the particle diameter. This is why smaller diameter particles cannot be used in a packed bed [14].

Integrating the ion exchange process with a membrane filtration in a hybrid process was reported to give a much higher efficiency and lower

process cost when compared with the fixed bed sorption method. A high efficiency in the process could be reached with sorbent beads with small particle sizes due to the increased surface area and enhanced kinetics [12,15]. It was reported that the high intensity of the process is achieved due to synergetic effects of sorbent concentrating at membrane vicinity [15]. According to the literature, the best results could be obtained when flux is maintained below critical value and when the permeate flux is fully synchronized with the sorption kinetics and rate of sorbent renewal on the membrane surface [15]. It was suggested that the retention time of the sorbent on the membrane surface could be controlled by various methods such as back-flush, cross-flow, reverse flow, pulsations, and gas sparging [15].

The sorption-membrane filtration hybrid method was especially tested for boron removal from geothermal water and seawater extensively [16–25]. Boron sorption was carried out by using commercially available ground boron selective chelating ion exchange resins. During the process, the boron loaded resin was filtered through submerged microfiltration (MF) or ultrafiltration (UF) membranes. In the published literature, it was reported that the resin beads were ground before they are employed in the hybrid process since the particle size of commercially available boron selective resins ranged from 0.2 to 1.0 mm. When the ion exchange resin beads were ground to an average particle size of 20 μm, this might cause some heterogeneity and irregular shape of particles and thus process sustainability might be badly influenced.

On the other hand, several procedures were reported in the literature for the preparation of small monodisperse polymer microparticles [26–31]. Membrane emulsification of monomers followed by suspension polymerization was defined as the simplest way to get the fine particles in the large scale [26,27]. Wolska and Bryjak synthesized the polymeric microspheres of poly(vinylbenzyl chloride-co-styrene-co-divinylbenzene) by this method and obtained microspheres with 25–30 μm of diameter [26]. The polymer beads were then functionalized with N-methyl-D-glucamine (NMDG) groups and they were tested in batch sorption of boron from an aqueous solution having 2 mg B/L. Although the authors mentioned that the sorption capacity of the synthesized resins was similar to that of commercially available boron selective ion exchange resins Purolite S108, Diaion CRB02, IRA-743 or Dowex-XUS-43594.00 with a sorption capacity of 0.8–1.0 mmol/g-resin, they implied that it was not possible to use all capacity of the resins due to the limited

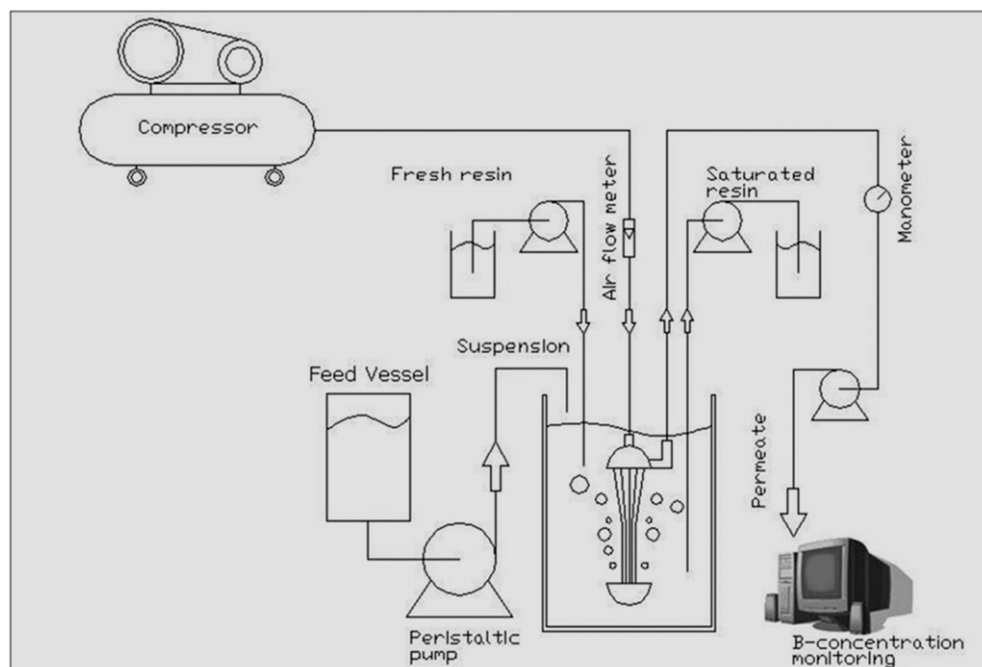


Fig. 1. The flow diagram of the hybrid system [21].

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