Desalination 437 (2018) 1–6

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

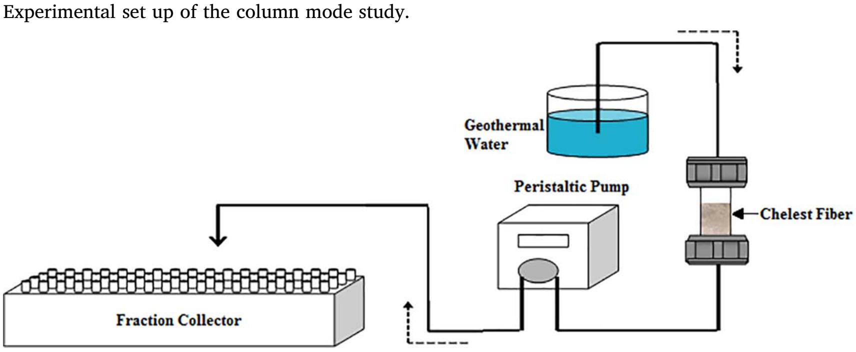
Packed bed column dynamic study for boron removal from geothermal brine by a chelating fiber and breakthrough curve analysis by using mathematical models

Yaşar K. Recepoğlu[a,d], Nalan Kabay[a,*], Idil Yılmaz Ipek[a], Müşerref Arda[b], Mithat Yüksel[a], Kazuharu Yoshizuka[c], Syouhei Nishihama[c]

[a] Ege University, Faculty of Engineering, Chemical Engineering Department, 35100 Izmir, Turkey
[b] Ege University, Faculty of Science, Chemistry Department, 35100 Izmir, Turkey
[c] The University of Kitakyushu, Faculty of Environmental Engineering, Department of Chemical Engineering, Hibikino 1-1, Kitakyushu 808-0135, Japan
[d] Izmir Institute of Technology, Faculty of Engineering, Department of Chemical Engineering, 35430 Izmir, Turkey

GRAPHICAL ABSTRACT

Experimental set up of the column mode study.



ARTICLE INFO

Keywords:
Boron
Chelest fiber
Geothermal brine
Packed bed column
Modified dose response (MDR) model
Thomas model
Yoon-Nelson model

ABSTRACT

In this study, the performance of *N*-methyl-D-glucamine (NMDG) type functional group attached a novel boron selective chelating fiber adsorbent, Chelest Fiber GRY-HW, was investigated for boron removal from geothermal brine containing 10–11 mg B/L through a packed bed column. The effect of feed flow rate (Space Velocity, SV) on breakthrough capacity of Chelest Fiber GRY-HW was studied using various SV values (15, 20 and 30 h^{-1}). The effect of SV on breakthrough capacity was particularly apparent when SV was decreased from 30 to 15 h^{-1}. Yoon–Nelson, Thomas and Modified Dose Response (MDR) models were applied to the experimental data to estimate the breakthrough curves and model parameters such as rate constants and breakthrough times. The obtained results showed that the breakthrough curves were better described by Modified Dose Response (MDR) model than those described by Yoon-Nelson and Thomas models in each case. Also, the model estimations for adsorption capacity obtained by MDR model agreed well with the experimental results.

1. Introduction

Although boron toxicity issue was first noticed by the farmers using post-treated product water for irrigation coming from a seawater reverse osmosis (SWRO) plant established in Eilat, Israel, in 1997, deboronation of aqueous mediums containing high boron concentration is

* Corresponding author.
E-mail address: nalan.kabay@ege.edu.tr (N. Kabay).

https://doi.org/10.1016/j.desal.2018.02.022
Received 22 October 2017; Received in revised form 21 February 2018; Accepted 22 February 2018

still a hot topic due to the harmful effects of boron to plants which have been clearly stated in the literature [1–6]. Consequently, strict standard values on the concentration of boron, such as 2.4 mg/L for drinking water and 1 mg/L for irrigation water, have been enforced by the environmental authorities [7]. There is not any unique method exists for boron removal from water. One or more methods can be applied based on the boron concentration in the medium. Adsorption onto fly ash [8], chemical precipitation [9], nanofiltration, reverse osmosis [10–16], electrodialysis [17], ion exchange-microfiltration [1,18,19], as well as ion exchange-ultrafiltration hybrid processes [2,20–22], electrodeionization [23] are some of the separation methods for boron.

The most extensively used technology for the removal of boron from aqueous solutions is the ion exchange using boron selective chelating resin [3,6,24–34]. The earlier studies on boron removal began with N-glucamine-type commercial resins, Diaion CRB 02 and Purolite S 108, using geothermal brine where Na^+, K^+, Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-} are major ionic components. Since geothermal brine has also certain salts, the effect of salinity on boron removal by those chelating ion-exchange resins in the presence of some salts such as sodium chloride and calcium chloride was also investigated. The results showed some decrease in the removal of boron from geothermal water in the presence of Ca, Na, and Cl ions. However, it was reported that the removal of boron was not influenced by an increase in the concentrations of these ions [24,25].

Nowadays, synthesis and advancement of new selective chelating resins and fibers with high selectivity, large capacity and fast sorption rate have received great attention notably for separation of boron from water [31–33,35,36]. However, adsorbents based on a natural polymer could be more preferable from the viewpoints of being eco-friendly materials. The branched-saccharide-chitosan resins to obtain a novel adsorbent derived from a natural polymer has been evolved and tested for boron removal [37]. Commercially available Chelest Fiber GRY-HW is one of a cellulose-based natural polymer which contains *N*-methyl-D-glucamine group. It has also been developed recently that this fibrous adsorbent found to possess a faster adsorption kinetic for boron than that of boron selective chelating ion exchange resins [35]. So far, we have compared the performance of Chelest Fiber with ion exchange resins, Diaion CRB 02 and CRB 05, by batch and column mode tests for removal of boron from geothermal brine [38]. Moreover, Ting et al. [39] evaluated the adsorption of boron from model solutions on new radiation grafted fibrous adsorbent containing *N*-methyl-D-glucamine [39]. Recently, a novel type poly (amic acid) (PAA) electrospun nanofiber membranes grafted with hyperbranched polyols were synthesized and used for the removal of boron from aqueous solutions [40].

Even though conducting those materials by batch adsorption is more appropriate for treatment of small volumes, it becomes an inconvenient method if there is a large volume to be treated due to overestimation of sorption capacities. Thus, utilization of them in a fixed bed column is more favorable in order to obtain more realistic laboratory results which has a great resemblance to the flow conditions in full scale constructed packed bed columns. In addition, a packed bed column dynamic study is important to anticipate the column breakthrough, which determines the functional life span of the column bed [41]. In this context, some models such as Yoon-Nelson model, Thomas model [41–44] and Modified Dose Response (MDR) model [41] were established to describe the dynamic behavior of adsorptive materials when packed into a column.

In this study, a novel chelating cellulose based fiber was used as adsorbent for the column-mode removal of boron from geothermal brine. The aim of the present investigation was to describe the packed bed column dynamic behavior of Chelest Fiber GRY-HW for sorption of boron from geothermal brine having certain salinity by applying three different mathematical models as a function of feed flow rate.

Table 1
Properties of Chelest Fiber GRY-HW.

Support material	Cellulose based fiber
True specific gravity	1.5
Water content (%)	< 45
Length of fiber (mm, approx.)	0.5
Diameter of fiber (µm, approx.)	100
Chelate amount (mmol/g)	1.3
Functional group	CH_3 (on N) CH_2-N-CH_2-$(CH(OH))_4$-CH_2OH (*N*-methyl-D-glucamine)

2. Experimental

2.1. Materials

Boron selective chelating ion exchange fiber, Chelest Fiber GRY-HW, was provided from Chelest Co., Japan. The properties of fiber adsorbent containing *N*-methyl-D-glucamine type functional group based on catalogue values are given in Table 1.

Geothermal brine obtained from Izmir Geothermal Co., Turkey was used in the experimental studies. The characteristics of geothermal brine sampled at different time periods were listed in Table 2.

2.2. Methods

A column of 0.7 cm diameter and 10 cm height packed with Chelest Fiber GRY-HW (wet wolume 0.5 mL) was used in chromatographic separation of boron from geothermal brine. The schematic view of experimental set up was given in Fig. 1. The geothermal brine was fed downward through the column at different space velocities (SV 15, 20 and 30 h^{-1}). A 3 mL (6 BV) of fractions were collected by the help of a peristaltic pump (ISMATEC model) and a fraction collector (both Advantec, CHF100SA and TELEDYNE ISCO). Elution was performed with a 5% of H_2SO_4 solution at SV 10 h^{-1} by collecting 2 mL (4 BV) of fractions. Boron concentration of samples was determined by Curcumine method at 543 nm using Jasco V-530 model uv–vis spectrophotometer.

3. Theory

The bed volume (*BV*, mL geothermal brine/mL fiber) was calculated from Eq. (1) [45]:

$$BV = \frac{Qt}{V} \tag{1}$$

where Q is feed solution flow rate (mL/min), t is operating time (min) and V is adsorbent wet volume (mL).

In addition, space velocity (*SV*, min^{-1} or h^{-1}) is the ratio of feed solution flow rate and adsorbent wet volume as in Eq. (2).

$$SV = \frac{Q}{V} \tag{2}$$

3.1. Yoon-Nelson model

A relatively straightforward model focused on the adsorption of gases or vapors in activated carbon was developed by Yoon-Nelson which depends on the rate of decrease in the possibility of adsorption for each adsorbate molecule being proportional to the possibility of sorbate sorption and the probability of sorbate breakthrough on adsorbent [44]. Yoon-Nelson equation is given as follows in Eq. (3):

$$\frac{C}{C_o} = \frac{\exp(K_{YN}t - \tau K_{YN})}{1 + \exp(K_{YN}t - \tau K_{YN})} \tag{3}$$