



Predicting the dynamics and performance of selective polymeric resins in a fixed bed system for boron removal



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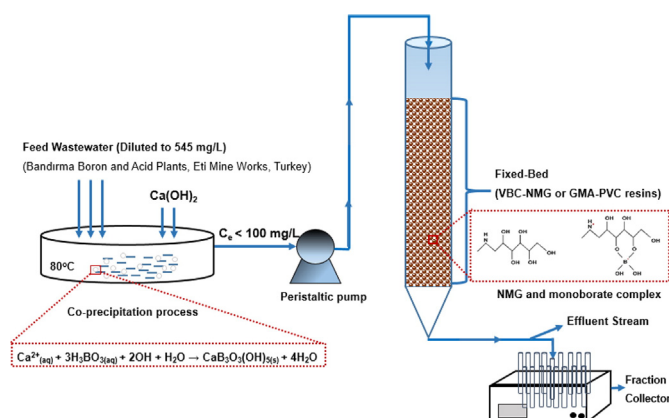
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HIGHLIGHTS

- Investigation and modeling boron adsorption data by applying kinetic models
- Modeling of fixed bed column data for boron removal by selective resins
- Predicting model parameters such as rate constants and breakthrough times
- Specific resins were easy to reuse.
- Applicability of resins to real wastewater sample obtained from mining industry

GRAPHICAL ABSTRACT



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ABSTRACT

The objective of the present study is to evaluate the boron removal performance of two selective resins: N-methyl-D-glucamine modified poly(styrene) based polymer (VBC–NMG) and the iminodipropylene glycol functionalized polymer (GMA–PVC). The effect of contact time on adsorption capacity was investigated in batch scale experiments. The adsorption kinetic data were fitted well with the pseudo-second-order model. Fixed bed column experiments were conducted at different flow rates. The breakthrough profile of VBC–NMG resin was found sharper than that of GMA–PVC. Column data were described using the Thomas and Yoon–Nelson models. The breakthrough curve prediction by the Thomas model was found to be very satisfactory for both resins. Applicability of selective resins to real wastewater obtained from mining industry was examined. The residual boron concentration in solution was reduced from 545 to less than 0.5 mg/L by the combination of precipitation–adsorption processes. Novel boron selective resins seem promising for practical uses as they could be used for more than eight cycles of recycling without any significant change in adsorption capacity.

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1. Introduction

In recent years, contamination of surface and subsurface waters with toxic heavy metals has become a growing environmental concern throughout the world. One of these toxic metals is boron, whose harmful effects make its presence in water a critical issue.

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Boron presents in groundwater or surface water in various locations where it occurs mainly in the form of boric acid. Common boron sources in water are urban wastewater containing detergents and cleaning products (washing powders and soaps), industrial effluents from a great number of industrial activities and diverse chemical products used in agriculture. Boron compounds are used in the glass and ceramic industry to produce borosilicate glass, insulation fiberglass, flame retardant fiberglass, ceramic glazes, neutron absorbers, porcelain enamels, herbicides or fertilizers [1,2]. The concentration of boron in water depends on the surrounding geological characteristics such as boron content of local geologic formations and anthropogenic sources. Seawater contains an average of 4.6 mg/L boron with a variation of concentration from 0.5 to 9.6 mg/L [3], while in freshwater, boron concentrations were detected as ranging from <0.01 to 1.5 mg/L [4]. In addition, boron levels found in surface water vary from less than 10 mg/L to greater than 1000 mg/L [5].

Although small quantities of boron are vital for the growth of plants and vegetation, elevated levels of boron may be injurious and even lethal to living organisms [6]. Boron contamination is a serious threat to crops as they are very sensitive to high levels of boron in the irrigation waters [7]. A vast amount of research has been undertaken to discover adverse effects of boron in animals. Long-term exposure to boron contaminated-water can result in many symptoms such as malfunctioning of the cardiovascular, alimentary, sexual and nervous systems of humans and animals [3,8]. Furthermore, chronic exposure to boron can cause deceleration of physical and intellectual progress of children, changes in blood composition and increases in the risk of the pathological births [6,9–11]. Although the World Health Organization (WHO) stipulated the maximum boron level in drinking water as 0.5 mg/L [12], the Boron Guideline Value of WHO was revised as 2.4 mg/L in 2011 [13]. On the other hand, the European Union (EU) recommends the maximum concentration of boron at 1 mg/L in drinking water [14].

Taking into account the increasing concentration of boron in waters, researchers have focused on the development of effective technologies for the removal of boron from contaminated-waters [3,7]. There are several methods suggested for boron removal from water and wastewater: precipitation-coagulation, reverse osmosis, electrodialysis, solvent extraction, membrane filtration, and adsorption (including ion exchange). Among these methods, adsorption has gained importance due to its simplicity and the availability of using many kinds of sorbents. The operation and efficiency of the adsorption are significantly related to an effective sorbent.

In recent years, boron-specific chelating resins have held much interest due to their selectivity and high capacity. The chelating resins with three or more hydroxyl groups, located in the *cis* position exhibit high selectivity to boron compounds. These resins can bind boric acid tightly by forming either neutral boron esters or borate complex anion with a proton as counter ion [1,2]. Several papers have focused on the strong adsorption affinity of boron to chelating polymers forming strong complexes. Parschova et al. [15] compared the performance of each sorbent possessing N-methyl-D-glucamine functional groups with different polymeric supports, polypropylene-styrene, polypropylene-GMA, viscose-GMA and commercially used polystyrene-DVB (Purolite D-4123). The breakthrough capacity of the synthesized resins was found much lower than the commercial BSR under the conditions investigated. Senkal and Bicak [16] demonstrated the boron chelating ability of iminodipropylene glycol and extended this boron chelate sorption onto polymer supported iminopropylene glycols. Kabay et al. [17] investigated boron removal from geothermal wastewater of Kizildere Geothermal Field by using N-glucamine-type chelating resin. They reported that the selective resin Diaion CRB02 could be used for ten sorption-washing-elution-washing-regeneration-washing cycles and the column-mode recovery of boron from acidic eluate solution was performed using a weak base anion exchange resin.

In the present paper, two boron selective sorbents were synthesized: (i) N-methyl-D-glucamine modified poly(styrene) based core-shell

type sorbent (VBC-NMG) and (ii) iminodipropylene glycol functionalized polymer (GMA-PVC). The effect of temperature and contact time on adsorption was investigated in batch scale experiments. The kinetic data of adsorption onto chelating resins were applied to the kinetic models, i.e., pseudo-first and pseudo-second orders, intra-particle diffusion and Elovich model. Fixed bed column experiments were conducted at different flow rates. Thomas and Yoon-Nelson models were applied to the experimental data in order to predict the breakthrough curves. Finally the boron removal efficiency of specific resins from a real wastewater sample was examined in the column-mode experiments.

2. Materials and methods

2.1. Chemicals and reagents

All the chemicals/reagents used in this work were of analytical reagent grade.

2.2. Preparation of N-methyl-D-glucamine functionalized VBC beads

The poly(vinyl-benzyl-chloride) (VBC) beads were prepared by suspension polymerization according to the method described in the literature [18]. Graft co-polymerization of glycidyl methacrylate (GMA) on the bead surface was achieved through benzyl chloride initiation sites of the poly(VBC). The poly(VBC-g-GMA) beads were then modified with N-methyl-D-glucamine as described in the previous study [19]. The resultant sample was coded as VBC-NMG.

2.3. Preparation of GMA-PVC sorbent

Graft polymerization of poly(glycidyl methacrylate) (GMA) beads was achieved through chlorine initiation sites on the crosslinked PVC by ATRP method and the poly(GMA) copolymer was modified with ethylenediamine according to the procedure described elsewhere. The resultant sample was designated as GMA-PVC [20].

2.4. Characterization

The Fourier transform infrared (FT-IR) spectra of the resins (before and after adsorption) were recorded on Perkin Elmer Spectrum One FT-IR Spectrometer between wavenumbers of 650–4000 cm^{-1} .

2.5. Adsorption kinetics

Adsorption is a time-dependent process and the rate of pollutant removed from aqueous solution is essential in order to design suitable sorption treatment plants. Moreover, the study of adsorption kinetics in wastewater treatment provides helpful insights into the mechanism of sorption reactions [21]. For kinetic adsorption experiments, 20 mg/L boron solution and defined amount of VBC-NMG and GMA-PVC adsorbents were contacted in a polyethylene bottle and the experiments were carried out at 25, 45 and 65 °C in order to calculate activation energy. Equilibrium boron concentration was analyzed with an atomic absorption spectrophotometer (Analytik Jena ContrAA 700 TR). The kinetics of boron adsorption onto chelating resins were described by four kinetic models, i.e., pseudo-first and pseudo-second orders, intra-particle diffusion and Elovich model.

Lagergren's first order rate equation is based on the concentration of the solution and adsorption capacity of solid and called as *pseudo-first order* [22]:

$$\frac{dq_t}{dt} = k_1 \cdot (q_e - q_t) \quad (1)$$

where q_e and q_t are the amounts of B adsorbed at equilibrium (mg/g) and at time t , respectively, and k_1 is the rate constant of pseudo-first

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