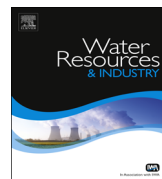




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Boron removal from water and wastewater using new polystyrene-based resin grafted with glycidol

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ABSTRACT

A divinylbenzene cross-linked polystyrene resin with amine functional groups (Purolite A170) was grafted with glycidol and characterized as a novel sorbent, GLY-resin, for the oxoborate removal from model solutions and post-crystallization lye. The sorption behavior of GLY-resin was investigated using a batch system. The results showed that the sorption was maximal at pH=9.5. The equilibrium was achieved after 24 h. Calculations based on Langmuir model show the monolayer sorption capacity $q_m = 1.3$ mg/g and the fitted experimental data chemisorption as a dominating mechanism of boron sorption on GLY-resin. Boron removal from the solution containing 5 mg B/L and post-crystallization lye having a 9.1 mg B/L was 99% and 80% respectively. The thermodynamic calculations indicated the spontaneous and endothermic nature of the sorption process. The pseudo-second-order model adequately described the boron sorption on GLY-resin. Sorption–desorption efficiency was 100%, which means the boron sorption at next cycle did not decrease.

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1. Introduction

Boron compounds have been detected in natural water at concentration levels of 0.3–100 mg/L. The concentrations above 100 mg/L depend on the surrounding geology and sewage disposal. Boron has also been found in drinking water at levels below 0.5 mg/L [1,2]. Boron is very important micronutrient for the plants, however, it is essential only in small quantities, and its excessive concentrations are damaging and

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even lethal to plants. In humans, small amounts of boron occur in all tissues. An excess of boron may lead to damage of the nervous system [3]. Therefore, boron concentration in water and wastewater is regulated in many countries. The recommended boron content in drinking water according to WHO guideline set in 1998, is 0.5 mg/L which was revised to 2.4 mg/L in 2011 [4]. According to the latest data, the value of 2.4 mg/L is probably acceptable for human; however, several types of crops are sensitive to boron at concentration below 2.4 mg B/L in irrigation water, e.g. 1 mg/L is definitely toxic dose for sunflower [2]. Thus, many countries (among them Poland) still implement their own standard [5]. The recommended content of boron in irrigation water and drinking water and wastewater discharged to the environment is 1.0 mg/L in Poland [6,7] and in the European Union [8].

The above limits cause that the removal of boron from aqueous solutions is of great environmental and public health concern. Biological treatment, chemical precipitation and conventional ion exchange are ineffective and phased out. Applicable methods are adsorption processes, membrane processes and hybrid processes. Among them the most hopeful method for the boron removal from aqueous solutions with boron content up to 100 mg/L is adsorption using hydroxyl-containing synthetic organic matrix [9].

Polystyrene is a polymeric matrix material commonly used for efficient preparation of ion-exchange resins [10,11]. In the case of boron-binding adsorbents, there is a need for introducing vicinal hydroxyl groups into the polymeric matrix to promote formation of tetracoordinated chelate complexes of boron [12]. Most synthesized resins have N-methyl-D-glucamine (NMDG) groups. The functional group is a polyol with five hydroxyls and a tertiary amine, which can offer more complexation sites, and form a stable complex with boron. These materials have a promising performance in boron removal process [2,13].

Since the 1990s more chelating resins with different functional groups have been developed. The chelating resins containing NMDG were prepared using glycidyl methacrylate–methyl methacrylate–divinyl benzene terpolymer (poly(GMA–MMA–DVB)), and poly(glycidyl methacrylate–co–trimethylolpropane trimethacrylate) (poly(GMA–co–TRIM)), and the silica–polyallylamine composites (SPC), and the cross-linked chitosan (CC), and the monodisperse poly(vinylbenzylchloride–co–divinylbenzene) (poly(VBC–co–DVB)), and poly(N-(4-vinylbenzyl)-N-methyl-D-glucamine) (P(VbNMDG)) as boron selective sorbents [14–19].

For last two decades the synthetic preparation of boron selective resins with different than NMDG groups has been examined [20]. Bicak and Senkal [21,22] synthesized a resin based on crosslinked polystyrene, modified with glycidyl groups and grafted with sorbitol, (the boron removal capacity was 13.18 mg/g) and a glycidyl methacrylate–methyl methacrylate–divinyl benzene terpolymer (poly(GMA–MMA–DVB)) with aminopropylene glycol functions, (the boron loading capacity of the resin was up to 32 mg/g). A cross-linked chitosan with multi-hydroxyl iminobis-(propylene glycol) functions (CCTS-IBPG), was prepared by Gazi et al. [23]. The boron removal ability of the resin was up to 29.19 mg/g, but the synthesis method of the resin was complex, not suitable for mass production. Yavuz et al. [24] modified poly(glycidyl methacrylate) grafted onto crosslinked PVC (DHPVC) with iminopropylene glycol groups. Some of these adsorbents, e.g. chelating chitosan – with NMDG, the P(VbNMDG) and CCTS-IBPG resins, had better performance and faster adsorption than the commercial resins [17,19,23]. Ince et al. [25] developed a solid tethered imino-bis-propanediol and quaternary amine functional copolymer (DADMAC) which was able to remove trace boron from aqueous solutions within less than a minute. Up to this day, the above-mentioned resins are not commercially produced. Probably they are not economical to implement on a larger scale. So the search for an effective sorption and regeneration process for the removal of boron is the current issue.

In this paper, divinylbenzene cross-linked polystyrene with secondary amine functionalized groups (Purolite A170) was the first time used as a support to synthesis of poly[4-N,N-bis(2,3-dihydroxypropyl)aminostyrene]. A new polystyrene-based resin containing vicinal hydroxyl groups named GLY-resin was characterized to determine its sorption properties toward oxoborate.

2. Experimental section

2.1. Materials

A basic standard solution of boron in the form of borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) – 1 g B/L; sodium hydroxide solution – 2 mol/L and 0.1 mol/L, hydrochloric acid solution – 1 mol/L and 2 mol/L,

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