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Modification of Crosslinked Poly(styrene) Based Polymers for Boron-Specific Extraction

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Summary: A new polymeric resin with glucose sulfonamide functions has been prepared for the extraction of boric acid. This poly (styryl sulfonamide) based resin has been demonstrated to be an efficient sorbent for the removal of boron. The resin had a boron loading capacity of 2.365 mmol.g^{-1} and showed reasonably rapid sorption ability. Splitting of sorbed boron can be achieved by simple acid leaching (2M H_2SO_4).

Keywords: boron removal; crosslinked resin; polymeric sorbent; sulfonamide

Introduction

Boric acid and borates are environmentally hazardous chemicals owing to their plant stunting effect, especially when present at levels of more than 4 ppm in irrigation water [1].

The most important boron source in the world is located in West Anatolia and the region around the boron mines from boron pollution. Wastes from the boron mines and the boric acid plants are the main sources of pollution.

The successful reports on the liquid-liquid extraction of boric acid using organic soluble vic-diols have appeared [2-4]. These methods are yet only applicable only to relatively concentrated boric acid solutions.

Removal of trace quantities of boric acid is a great problem; the more an increasing trends in boron levels in rivers have become alarming owing to the extensive use of various perborate formulations as detergent additives.

Removal of boron by chelating bases on the use of vic-diols that form stable chelates with boric acid and its salts under aqueous conditions. Molecules with three or more hydroxyl groups can

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react to form either anionic boron esters or borate complexes. Having 6 hydroxyl functions, sugar derivates such as mannitol and sorbitol have high boron binding capabilities. In accordance with this key principle, poly(styrene)-based resins with N-methyl-D-glucamine functions, emerged in the mid 1960'[5], are boron specific sorbents. This resin has excellent efficiency in boron uptake although some loss of activity is observed in regenerations by acid [6].

In our previous study, crosslinked polystyrene sulfonamide with sorbitol functions has been proven to be regenerable without loss of activity in boron sorptions [7].

In a related study, Japanese workers demonstrated that additional amine functionality is essential for high levels of boron chelation [8]. Apparently, the role of the amine function is the capture of protons formed by diol complexes of boron.

Based on this principle, in our recent studies, we have developed two glycidyl methacrylate based polymers with N-methyl-D-glucamine functions starting either from monomers [9] or from a crosslinked polymer [10]. These polymers are efficient and regenerable in boron sorption.

In searching for new functional polymers for chelation with boric, we have noticed that crosslinked poly(styrene)-based glucose sulfonamides have a structure suitable for boron removal. Since sulfonamide groups do not hydrolyze readily by acid treatments, this material is re-usable.

In the present study, we have prepared glucose sulfonamide containing polymeric sorbents in one step starting from chlorosulfonated poly(styrene) resin. Boron uptake ability and regeneration conditions of the resulting polymer sorbent have been investigated.

Experimental

Materials

All chemicals used were analytical grade: Styrene (Fluka), DVB (Aldrich, 55% mixtures of m- and p- isomers, the remainder is 3-and 4- ethyl vinyl benzene), glucamin hydrochloride (Fluka), boric acid (Aldrich), sorbitol (Fluka), carminic acid (Merck). H_2SO_4 (Riedel), chlorosulfonic acid (Fluka). They were used as supplied.

Preparation of the chlorosulfonated PS-DVB Beads

The preparation of the crosslinked PS-DVB (%10 mol/mol) beads and their chlorosulfonation were performed according to previously procedures [11].

Determination of the degree of chlorosulfonation

0.2 g of the chlorosulfonated polymer were added to (20 ml) of 10 % NaOH solution and refluxed for 4h. The mixture was filtered, the filtrate and washings were transferred to a volumetric flask and diluted properly. The chloride content of the solution was assayed by the mercuric thiocyanate method [12]. This gave a final degree of chlorosulfonation of 3.5 mmol.g^{-1}.

Reaction with glucamine hydrochloride

10 g of the chlorosulfonated polymer were added portionwise to a stirred solution of glucamine hydrochloride (11g , 0.051 mol) in NMP (50 ml) at 0 ^{0}C. The mixture was shaken for 6 h at room temperature, poured into 300 ml of water, and filtered. After being washed several times with water, the beaded product was the dried at 50 ^{0}C for 8 h in vacuum. The yield was 10.7 g.

Determination of the sulfonamide content

For the determination of the sulfonamide content, 0.5 g of the sample were interacted with 1.5 g of KOH in 15 ml of water for 24 h. After filtration, 3 ml of the filtrate were diluted to 25 ml with distilled water and titrated with 0.4 M HCl solution. By comparing with the result for the unreacted solution, the sulfonamide content was found to be 2.38 mmol.g^{-1}, indicating 98.3 % conversion of chlorosulfone groups.

Determination of the boron loading capacity

Maximum loading capacity of the resin was determined by interaction of 0.3 g of the polymer sample with an aqueous solution 20 ml, (0.5M) of H_3BO_3 for 24 h. After filtration, the boron content was determined analytically based on 5 ml of the filtrate transferred in 10 ml of 0.5 M sorbitol solution using phenolphthalein as color indicator, as described before[10].

The sorbed amount was obtained by differentiation of boron contents of the interacted and noninteracted boron solutions.

This experiment indicates that the boron-loading capacity is 2.365 mmol.g^{-1} resins.

Boron sorption kinetics of the resin

Batch kinetics experiments were carried out using 5.10^{-3} M boric acid solution as follows:

The resin (1g) was interacted with 100 mL of boric acid solution (5.10^{-3} M). The mixture was stirred with a magnetic bar. Five milliliters of aliquots were taken at appropriate time intervals and filtered. Residual boron contents of the filtrates were determined colorimetrically (λ =585nm) by the carminic acid method [13]. The data derived were used to build up the concentration-time plots in Fig.1.

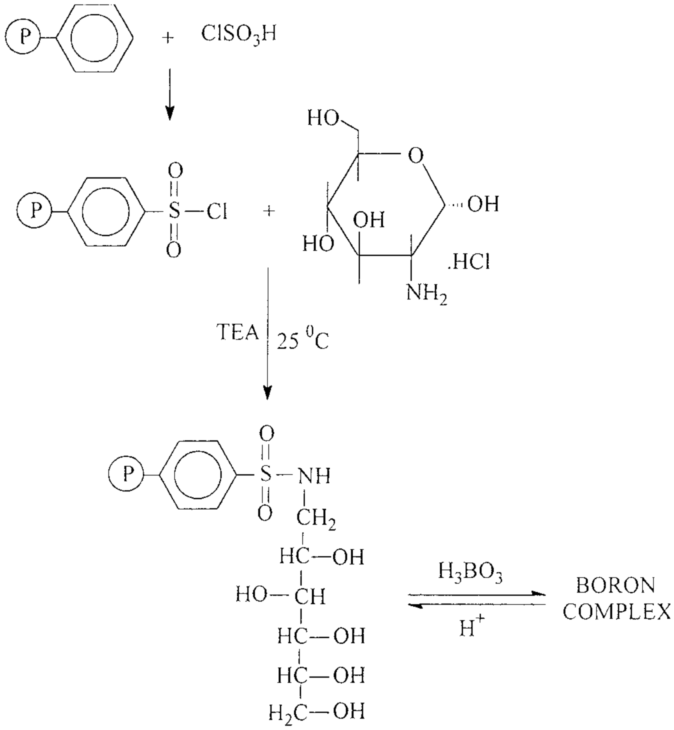
Desorption of boron from loaded samples

Boron loaded polymer samples (approximately 0.2 g of each) were desorbed by treatment with 10 mL of H_2SO_4 (2 M) for 24 h, at room temperature.

Desorbed boron in the filtered acidic solution was assayed by titrimetric method as described above. This analysis gave 2.254 mmol boron per g of the loaded polymer.

Results and Discussion

In the present work, an alternative boron specific sorbent has been developed according to the reaction pathways as depicted in Scheme 1. In the first step, resin was prepared by copolymerization of styrene with DVB. The polymerization was carried out using suspension polymerization methodology using toluene as diluent and water as continuous phase. Crosslinked polystyrene beads were chlorosulfonated using chlorosulfonic acid. Chloride analysis of the product in the first step (3.5 mmol.g^{-1}) revealed a degree of chlorosulfonation of the phenyl rings of ~ 63.2%. The second step was performed with essentially quantitative conversion of the chlorosulfonyl groups when excess of glucamine hydrochloride was used. The sulfonamide content of the resulting resin was calculated as 2.38 mmol.g^{-1}.



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Boron Uptake

Batch extraction experiments have been carried out to investigate the boron uptake ability of the polymer resin. In all experiments, 210-420 µm size fraction has been used. In the batch experiment, the resin sample was simply soaked with 0.5 M boric acid solution. By analysis of unreacted boric acid in the solution, the capacity of the resin was calculated as 2.365 mmol.g^{-1}. In these experiments we have used non-buffered solutions deliberately to simulate practical conditions of applications.

Kinetics of boron sorption

Kinetics of boron sorptions were recorded by batch kinetic experiments as follows: 1 g of the modified resin was soaked in 100 ml of H_3BO_3 solution ($5.\ 10^{-3}$ M). While stirring at room temperatures, 5 ml samples were taken out at appropriate time intervals to follow the concentration of boron remaining un-reacted in the solution. Based on these data, the time-dependence variation of boron sorption was plotted, as shown in Fig. 1. Kinetic experiments show that sorption of boron from aqueous solutions is reasonably fast.

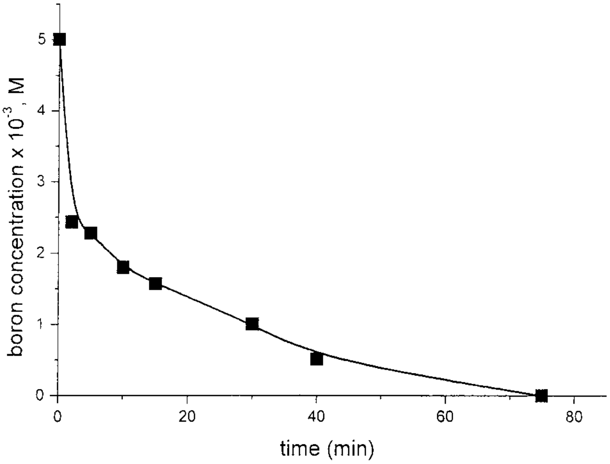

Fig.1. Concentration-time plots of the diluted boron solutions ($5.\ 10^{-3}$ M) contacting with 1 g. of polymer sample

Recovery of boric acid

When loaded polymer samples were treated with 2 M H_2SO_4, 2.254 mmol boric acid were recovered from 1 g of the resin. Taking into consideration mass increase by boron sorption this amount accounts for about 98.3 % of the capacity. However, second acid treatment gives boron free polymer. In other words, repeated acid treatment is necessary for complete recovery of boric acid.

In order to test boron uptake ability of the regenerated polymer, loading experiment was repeated at the same conditions. The capacity of the recycled polymer was found to be 2.31 mmol.g^{-1} which is very close to the original capacity (2.365 mmol.g^{-1}).

Conclusion

The glucosulfonamide-modified resin exhibits reasonable efficiency in the extraction of boric acid from water. The material can be prepared from simple reagents and can be regenerated without significant loss of the capacity.

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