Boron Removal from Water and Wastewater using New Polystyrene-Based Resin Grafted with Trometamol and 3-Amino-1,2-propanediol

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Summary: Boron is one of the significant micronutrients for the plants; however, its excessive concentrations are lethal to plants. The accumulation of boron may cause damage to the liver, kidney, nervous system, respiratory system, digestive system, reproductive system and even threaten human life. Researchers consider using different methods to prepare boron chelating resins. In this work, two innovative, facile, and low-cost methods were developed to prepare polystyrene-alcohol resins. The KDN and KLA resins had the highest adsorption capacity for boric acid in an aqueous solution at 288 K ,and the adsorption capacity was 36.17 mg·g-1 and 43.47 mg·g-1, respectively. The desorption percentages of boric acid on KDN and KLA resins were 90.75 % and 90.32 % respectively, by using 1 mol·L-1 HCl as an eluent. Therefore, KDN and KLA resins have the characteristics of a simple experimental process, large adsorption capacity, high elution rate, reusable, and low production cost. Therefore, it has a high commercial value and development prospects.

Key words: Trometamol; 3-Amino-1,2-propanediol; Boric acid; Adsorption; Desorption.
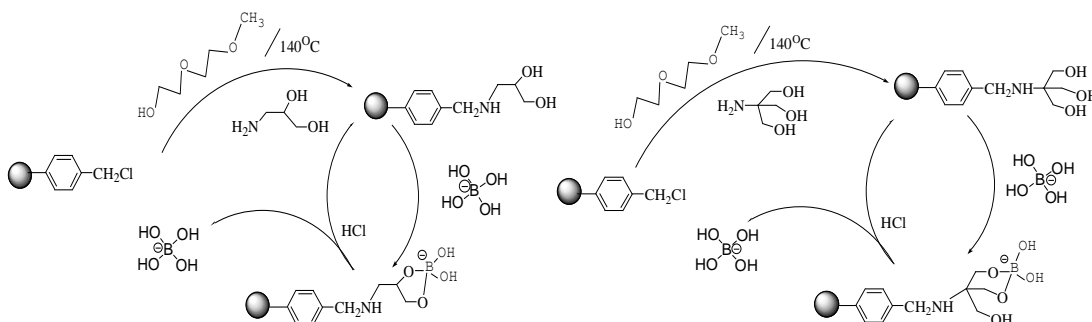
Introduction

Boron is extensively dispersed in industry and agriculture. Borax can be produced as a raw material in chemical or as metallurgical industry. Boron is one of the significant micronutrients for the plants; however, its excessive concentrations are lethal to plants [1]. The accumulation of boron may cause damage to the liver, kidney, nervous system, respiratory system, digestive system, reproductive system and even threaten human life [2]. Most of the boron for plants come from the soil, and the content of boron in the soil is crucial. Therefore, the water used in irrigation needs to maintain the best boron content. Excess of boron in water may come from medicine, metal smelting, detergent, etc. Boron removal from wastewater has become an urgent problem to be solved. The main methods for extracting boron from aqueous solutions are chemical precipitation, reverse osmosis, extraction, acid crystallization, fractional crystallization, adsorption, Taguchi method, etc [3-11]. However, the most widely followed method employs ion-exchange resins.

Researchers consider using different methods to prepare boron chelating resins. The boron chelate resin that has been reported is the meglumine-based boron chelate resins [12-15], the glycidyl boron chelate resins [16-17], the salicylic acid boron chelate resins [18], the tannic acid boron chelating resins [19] and the catechol boron chelating resins [20], had the highest adsorption capacities for boric acid, which were 35.13 mg·g-1, 42.16 mg·g-1, 14.7 mg·g-1, 6.92 mg·g-1 and 24.3 mg·g-1, respectively. IRA743 resin was widely used in factories; however the experimental process was

complicated and took a long time, the raw materials are toxic and expensive. In this work, two innovative, facile, and low-cost methods were developed to prepare polystyrene-alcohol resins. Chloromethylated polystyrene resin was modified by 3-amino-1,2-propanediol to obtain dihydroxyamine resin (KLA resin); Using trometamol as a raw material, chloromethylated polystyrene resin was modified to prepare polyhydroxyamine resin (KDN resin). The proposed method opens up a new direction for the synthesis of boron chelate resin and reduces the cost of boron removal resin. Therefore, KDN and KLA resins have the characteristics of a simple experimental process, large adsorption capacity, high elution rate, and low production cost. Therefore, it has a high commercial value and development prospects.

Experimental

Reagents and Apparatus

The following reagents of analytical grade, trometamol, 3-Amino-1,2-propanediol, 2-(2-Methoxyethoxy)ethanol, boric acid, 8-Amino-1-naphthol-3,6-disulfonic acid monosodium salt monohydrate, ammonium acetate, ethylenediaminetetraacetic acid disodium salt, ascorbic acid, salicylaldehyde, potassium nitrate, sodium hydroxide, silver nitrate, ammonium thiocyanate, sodium nitrate, hydrochloric acid, and absolute ethyl alcohol were used.

Fourier Transform infrared spectroscopy (Thermo Nicolet Corporation), UV-4802 double-beam UV-Vis Spectrophotometer (Unico Instrument Co., Ltd), SHA-2000 digital display full temperature water bath oscillator (Changsha Soto Scientific Instrument Equipment Co., Ltd) and Electronic analytical balance (Shanghai Mingqiao Instrument Co., Ltd) were employed.

Preparation of KDN resin and KLA resins

2-(2-Methoxyethoxy)ethanol was used as a solvent to swell chloromethylated polystyrene resin (Cl-PS-PVB) for 8 h. Then 2-(2-Methoxyethoxy)ethanol and trometamol were added into a 3-neck boiling flak, stirred to dissolve, and chloromethylated polystyrene resin was added. The above mixture was reacted for 24 h at 140 °C. The obtained product was then extracted for 10 h with ethyl alcohol and dried at 60 °C to obtain KDN resin. Synthesis route of KDN resin was show in Fig. 1
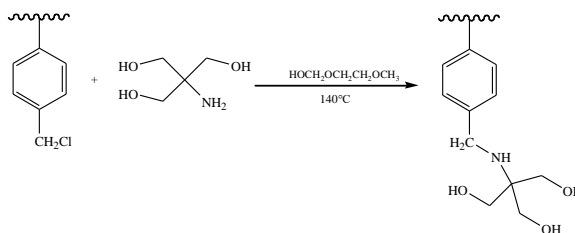

Fig. 1:   Synhesis route of KDN resin.

Then 2-(2-Methoxyethoxy)ethanol and 3-amino-1,2-propanediol were added into a 3-neck boiling flak, stirred to dissolve, and Cl-PS-PVB was added. The above mixture was reacted for 24 h at 140 °C. The obtained product was then extracted for 10 h with ethyl alcohol and dried at 60 °C to obtain KLA resin. Synthesis route of KLA resin was show in Fig. 2
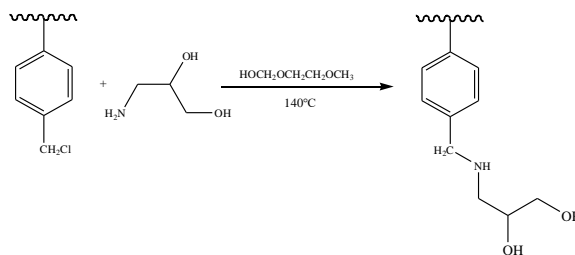

Fig. 2:   Synhesis route of KLA resin.

Method for the preparation of color developing reagent

2 g of 8-Amino-1-naphthol-3,6-disulfonic acid monosodium salt monohydrate was weighed into a beaker, added with 5 ml of deionized water and 0.1 ml of HCl (1+4) and was then stirred. Then, a mixture of 0.6 ml of salicylaldehyde and 0.6 ml of absolute ethyl alcohol was added and stirred for 30 min, and kept overnight. The obtained solid products were washed several times with absolute ethyl alcohol until they become light yellow, separated by filtration, and then dried at 100 °C for 24 h to obtain methanimidic acid.

Method for the quantitative analysis of boric acid

0.5 ml of a saturated solution of ethylenediaminetetraacetic acid disodium salt, 2.5 ml of HCl (1+4), 5 ml of ammonium acetate solution (500 g·L^{-1}), 6 ml of color-developing reagent, and an appropriate amount of boric acid solution were added

into a volumetric flask of 50 ml. Then, deionized water was added to make up 50 ml, and the resulting solution was left for 6 h, and then its absorbance was measured.

Resin structure

The infrared absorption spectra of KDN and KLA resins were determined using Avatar 370 Fourier transform infrared spectrometer. The specific surface, pore volume, and pore size of KDN and KLA resins were determined by Tristar 3000 fully automatic BET specific surface area and pore analyzer. The water content of KDN and KLA resins were determined according to the national standard GB5757-2008. The chlorine content of KDN and KLA resins were determined according to the methods of Volhard.

Adsorption of boric acid in aqueous solution on KDN and KLA resins

Static adsorption: 10 dry plastic bottles were divided into two groups (5 in each group). 0.5 g of KDN and KLA resins were weighed into each group of plastic bottles. 25 ml of different concentrations of an aqueous solution of boric acid was accurately transferred to each plastic bottle. The plastic bottles were kept in a water bath thermostat ($110 \, r \cdot min^{-1}$) and were shaken for 24 h at 288 K, 298 K, 308 K, 318 K. After the resin reached the adsorption equilibrium, the absorbance of boric acid was measured. Then, the equilibrium concentration (c_e) and the adsorption amount (q) were calculated using the appropriate equation.

Dynamic adsorption: Using a graduated cylinder, 10 ml of wet synthetic resin, was measured and filtered with a Buchner funnel. Then, using a filter paper to absorb water on the resin surface and then weighed. The resin was then transferred to the chromatography column. Using a certain concentration of an aqueous boric acid solution as the upper column liquid, the flow rate was set to $2 \, BV \cdot h^{-1}$, and the concentration of boric acid in the effluent was detected until it is the same as the concentration in the upper column liquid.

Dynamic desorption: The residual aqueous boric acid solution on the resins was washed with 4 BV deionized water until there is no boric acid in the effluent. Using $1 \, mol \cdot L^{-1}$ HCl as the upper injection liquid, the flow rate of the device was set to $2 \, BV \cdot h^{-1}$, and the concentration of boric acid in the outflowing liquid was checked until its concentration becomes zero.

Result and Discussion

IR analysis

The IR spectra of Cl-PS-PVB, KDN and KLA resins are shown in Fig. 3, In the spectra of KDN, the new absorption peaks appearing at 1034 cm^{-1} originated from the characteristic vibrations of primary amine. In the spectra of KLA, the new absorption peaks appearing at 1034 cm^{-1} and 1104 cm^{-1} originated from the characteristic vibrations of primary amine and secondary amine, respectively. In the spectra of Cl-PS-PVB, the absorption peaks for the characteristic vibrations of C-Cl disappear from 672 cm^{-1}. These results showed that trometamol and 3-Amino-1,2-propanediol were successfully bonded to chloromethyl groups of Cl-PS-PVB.

Performance analysis

The performance analysis of Cl-PS-PVB, KDN, and KLA resins is shown in Table-1. It could be noted that the chlorine content of KDN and KLA resins are lower than Cl-PS-PVB resin. The weak base exchange amount of KDN and KLA resins were 2.57 $mmol \cdot g^{-1}$ and 3.33 $mmol \cdot g^{-1}$, respectively. The results showed that trometamol and 3-Amino-1,2-propanediol were successfully bonded to chloromethyl groups of chloromethylated polystyrene resin. BET surface area of KDN and KLA resins were lower than Cl-PS-PVB resin. Pore volume and pore size of KDN and KLA resins were higher than Cl-PS-PVB resin. This may be due to that the resin is swollen with methyl diglycol before the reaction, and the partial pore volume is not entirely shrank owing to the embedding of trometamol and 3-amino-1,2-propanediol molecules.

Table-1:   Performance analysis of resin.

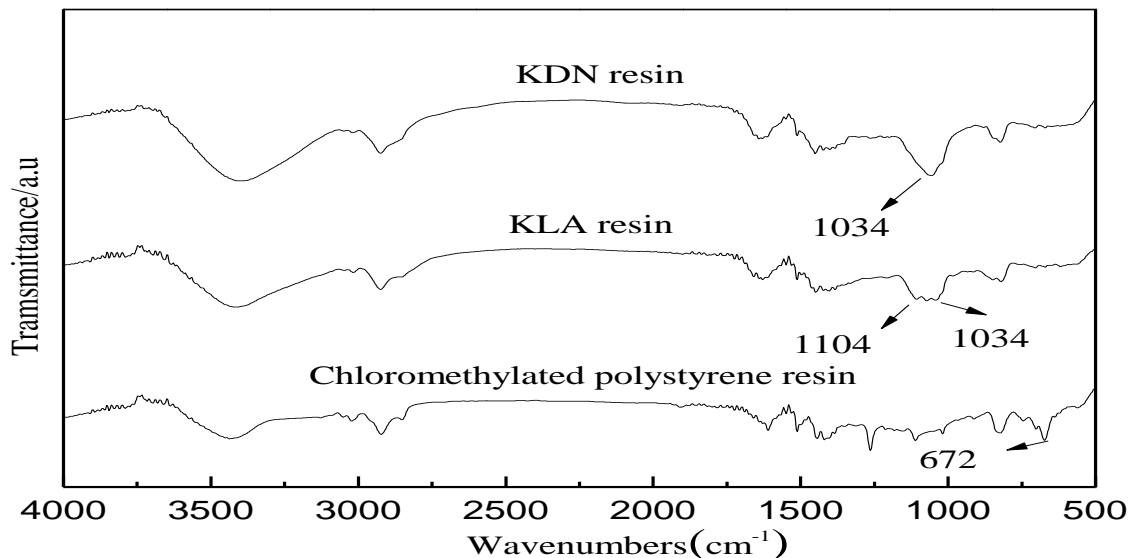| resin	chlorine content	water content	weak base exchange	BET surface area	pore volume	pore size
	/ %	/ %	/(mmol·g⁻¹)	/ (m²·g⁻¹)	/ (cm³·g⁻¹)	/ (nm)
Cl-PS-PVB	16.5	39.18	/	40.3609	0.131954	27.2197
KDN	4.60	46.41	2.57	32.6589	0.134167	40.0307
KLA	3.61	48.01	3.33	35.8806	0.136321	40.0376

Fig. 3 IR spectra of KDN resins and KLA resins.

The Freundlich adsorption isotherms and the Langmuir adsorption isotherms of boric acid on KDN and KLA resins were shown in Fig. 4 and Fig. 5, respectively. It can be seen that the adsorption capacity of boric acid on KDN and KLA resins increased with equilibrium concentration and decreased with the increase of temperature. The results showed that the adsorption of boric acid onto the resins from aqueous solution is an exothermic process. The KDN and KLA resins had the highest adsorption capacity for boric acid in an aqueous solution at 288 K ,and the adsorption capacity was 36.17 mg·g^{-1} and 43.47 mg·g^{-1}, respectively.
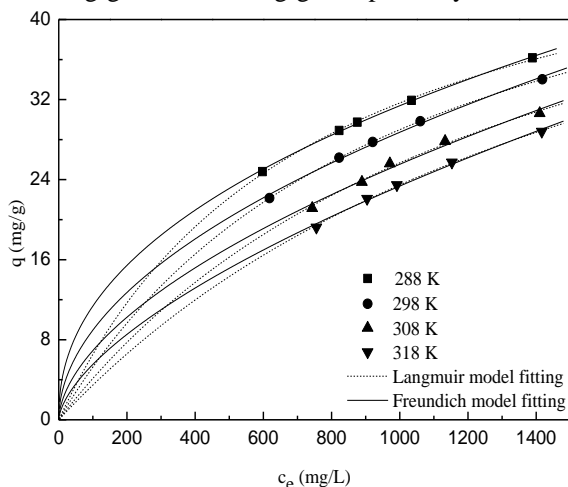
Table-2 and 3 show the adsorption model parameters of KDN and KLA resins on the aqueous solution of boric acid obtained by fitting the experimental data according to Freundlich isotherm equation (1) and the Langmuir equation (2), respectively. It can be seen from the table that, compared with the Freundlich adsorption model, the Langmuir adsorption model has a larger correlation coefficient R^2. The Langmuir adsorption model is more in line with KLA and KDN's adsorption on the aqueous solution of boric acid, which belongs to the monolayer adsorption.

$$q = kc_e^{\frac{1}{n}} \tag{1}$$

$$\frac{c_e}{q} = \frac{c_e}{q_m} + \frac{1}{K_L q_m} \tag{2}$$

where q is adsorption capacity, c_e is equilibrium concentration, on, n the coefficient "n" in the Freundlich isotherm equation, k the constant in the Freundlich isotherm equation, q_m the saturated adsorption capacity, K_L the constant in the Langmuir isotherm equation

Fig. 4:   Adsorption isotherms of boric acid on KDN
          resin.

Table-2:   Adsorption isotherm model parameters of boric acid on KDN resin.

T	Langmuir model			Freundlich model		
(K)	q_m (mg/g)	$K_L/10^{-3}$ (mg/L)	R^2	K_F [(mg/g) (L/mg)$^{1/n}$]	1/n	R^2
288	55.3120	1.3400	0.9972	1.4903	0.4412	0.9983
298	58.0721	0.9974	0.9999	0.8710	0.5061	0.9943
308	61.1200	0.7245	0.9904	0.5072	0.5672	0.9799
318	65.2330	0.5621	0.9977	0.3107	0.6254	0.9921

Table-3:   Adsorption isotherm model parameters of boric acid on KLA resin.

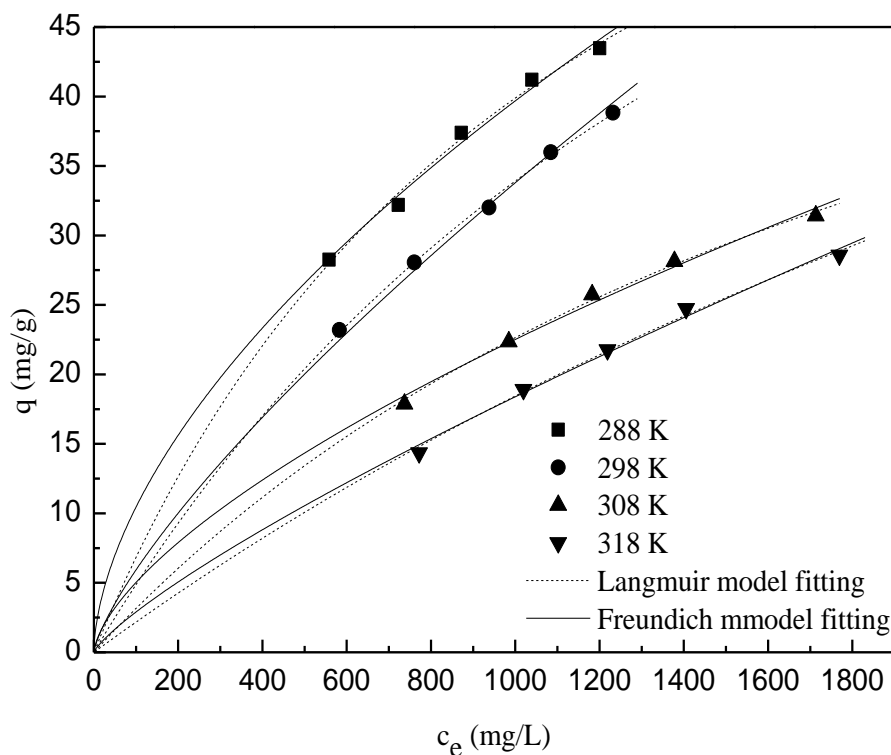| T	Langmuir model			Freundlich model		
(K)	q_m (mg/g)	$K_L/10^{-3}$ (mg/L)	R^2	K_F [(mg/g) (L/mg)$^{1/n}$]	1/n	R^2
288	86.4363	0.8568	0.9885	0.7258	0.5793	0.9848
298	100.5378	0.5091	0.9973	0.1829	0.7556	0.9974
308	72.3667	0.4556	0.9950	0.2505	0.6512	0.9854
318	109.4889	0.2026	0.9938	0.0723	0.8018	0.9888

Fig. 5:   Adsorption isotherms of boric acid on KLA resin.

Dynamic adsorption and desorption of boric acid solution on KDN resin and KLA resins

The dynamic adsorption curves of boric acid on KDN and KLA resins are shown in Fig. 6. When the initial concentration of the boric acid is 1904.59 mg·L^{-1}, the leakage adsorption capacity of KLA resin for boric acid is 10.25 mg·g^{-1} within 2 BV, and the saturated adsorption capacity of KLA resin for boric acid is 44.14 mg·g^{-1} within 16 BV. When the initial concentration of boric acid was 1628.98 mg·L^{-1}, the leakage adsorption capacity of KDN resin for boric acid was 8.63 mg·g^{-1} within 2 BV, and the saturated

adsorption capacity of KDN resin for boric acid was 32.57 mg·g^{-1} within 14 BV. The dynamic desorption curves of boric acid on KDN and KLA resins are shown in Fig. 7. The desorption percentages of boric acid on KDN and KLA resins were 90.75 % and 90.32 % respectively, by using 1 mol·L^{-1} HCl as an eluent. This shows that KDN and KLA resins have the characteristics of large adsorption capacity, high elution rate.
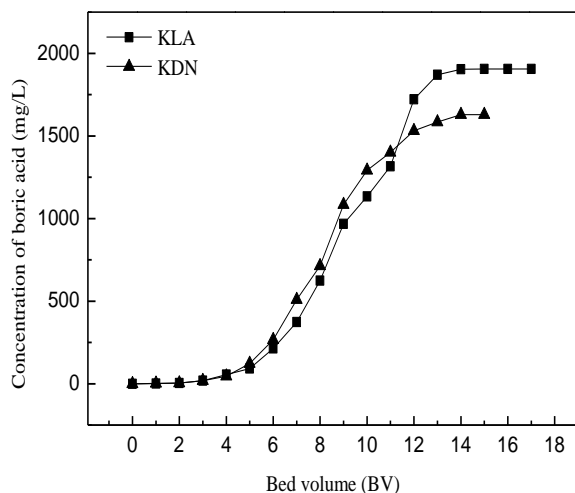
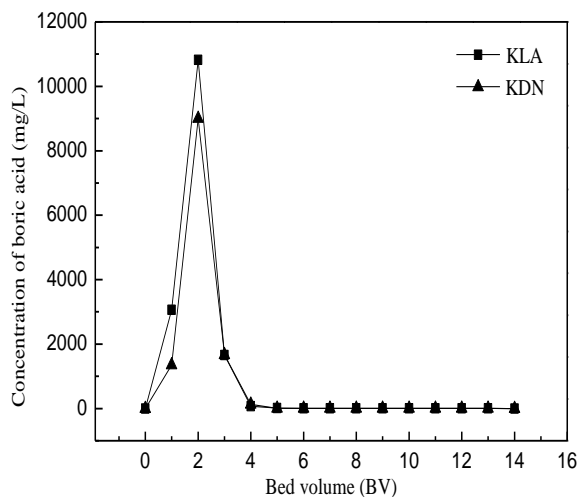Fig. 6:   Dynamic adsorption curve of boric acid.

Fig. 7:   Dynamic desorption curve of boric acid.

Mechanism of boric acid complex formation with polyol

The mechanism of boric acid complex formation with polyol is shown in Fig. 8. In an aqueous solution, at first, boric acid converts into $B(OH)_4^-$ and then complexes with a polyhydroxy group in two steps. The pair of hydroxyl groups of $B(OH)_4^-$ complexes with polyhydroxy groups, the resulting material of which has a stronger ability to complex, and thus the other pair of hydroxyl groups of $B(OH)_4^-$ could continue to complex with the polyhydroxy groups. [21]
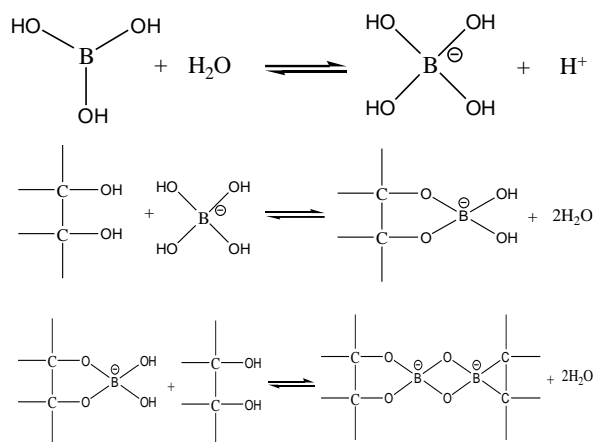

Fig. 8: Mechanism of boric acid complex formation with polyol.

Conclusion

KLA and KDN resins were prepared via the reaction of chloromethylated polystyrene resin with 3-Amino-1,2-propanediol and trometamol, respectively. The chemical characterization showed that the alcohols were successfully bonded to polystyrene resin. The results study demonstrated that for the adsorbates with an initial concentration of 1700 $mg \cdot L^{-1}$ at 288 K, in which the KDN and KLA resins had the highest adsorption capacities for boric acid, which were 36.17 $mg \cdot g^{-1}$ and 43.47 $mg \cdot g^{-1}$, respectively. The desorption percentage for boric acid was 90.75 % and 90.32 %, respectively. The KDN and KLA resins have the characteristics of a simple experimental process, large adsorption capacity, high elution rate, and low production cost. It has a high commercial value and development prospects.

Acknowledgements

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