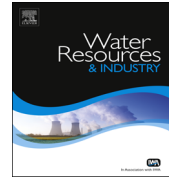




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## Boron removal from water and wastewater using new polystyrene-based resin grafted with glycidol



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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,

ammonia aq. 5% (w/w). All reagents were analytically pure and supplied by POCh situated in Gliwice (Poland). Purolite A170, a macroporous polystyrene-divinylbenzene resin functionalized with complex amine groups was supplied by Radus (Częstochowa, Poland) and glycidol – 96% (w/w) was purchased from Acros Organics (Gliwice, Poland).

## 2.2. Apparatus and laboratory equipment

A spectrophotometer ICP-OES Varian 710 (VARIAN), a FT-IR spectrophotometer Nicolet 6700 (Thermo Scientific), Labmate volume pipettes (PZ HTL, Warsaw), a WU-4 universal shaker (PREMED, Warsaw); a WPE 120 electronic balance (Radwag, Radom); an analytical balance WPA 60/C (Radwag, Radom), a MILL-547 shaker with heating bath (AJL ELEKTRONIC), pH-meter Basic 20+ (CRISON); laboratory glassware and small equipment: conical flasks with ground glass joint, measuring flasks, beakers and chemical funnels.

## 2.3. Synthesis of GLY-resin

Purolite A170 (2 g), a macroporous weakly basic anion resin crosslinked with divinylbenzene and functionalized with amine complex, was pre-washed with distilled water (50 mL) and dried at room temperature to a constant weight. Next, 50 mL of HCl was added and stayed for 3 h. The liquid was decanted and resin was dried to a constant weight and placed in the three-necked flask with the heating jacket. Then, a 20 mL of glycidol was added, and the resulting mixture was heated below 120 °C for 6 h and cooled in case event of temperature increase. Next, the resin was filtered, washed with distilled water (50 mL) five times and dried at room temperature to a constant weight. 2.6 g of GLY-resin was obtained.

The formation of the GLY-resin films was studied by IR spectroscopy, with a Thermo Scientific Nicolet 6700 FT-IR spectrophotometer using attenuated total reflectance (ATR method).

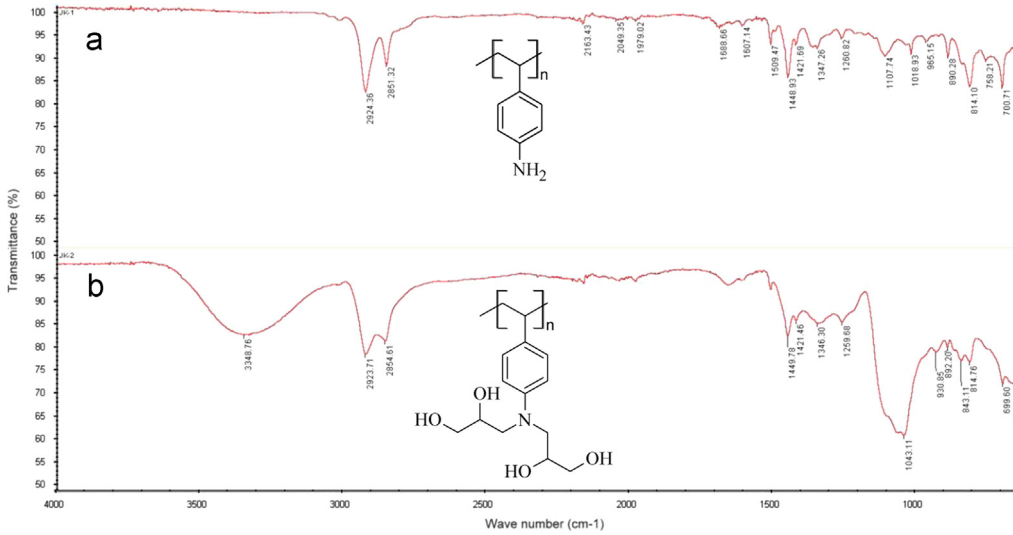
## 2.4. Post-crystallization lye

Post-crystallization lye was taken from Desalination Plant. Its pH was 7.1. The composition of post-crystallization lye was as follows: Cl<sup>-</sup> (215 g/L), Br<sup>-</sup> (1.1 g/L), I<sup>-</sup> (83 mg/L), NO<sub>3</sub><sup>-</sup> (304 mg/L), NO<sub>2</sub><sup>-</sup> (26 mg/L), SO<sub>4</sub><sup>2-</sup> (555 mg/L), H<sub>3</sub>BO<sub>3</sub> (519 mg/L), SiO<sub>2</sub> (0.32 mg/L), Li<sup>+</sup> (57 mg/L), Na<sup>+</sup> (98.2 g/L), K<sup>+</sup> (5.7 g/L), Mg<sup>2+</sup> (19.2 g/L), Ca<sup>2+</sup> (7.3 g/L), and Sr<sup>2+</sup> (307 mg/L).

## 2.5. Methods

A series of the batch-mode sorption studies were conducted to evaluate the effects of the initial boron concentration, pH level, temperature, time and GLY-resin dose on boron sorption. The experiments were carried out with 0.05–0.3 g of resin and 25 mL of boron solution of concentration 4–30 mg B/L in the pH range of 3.0–10.0 (adjusted by addition of 1 M HCl or 5% ammonia solution) at 20–60 °C temperature for 2–24 h in 250-mL conical flask with a ground glass joint. 25 mL of diluted post-crystallization lye (lye-to-distilled water voluminal ratio=1/10) was contacted with various amounts of resin (0.05, 0.10, 0.15, 0.20, and 0.25 g) for 24 h at 25 °C under pH ca. 9.5. Then, boron solution (or real medium) and resin beads were shaken at 120 rpm mixing rate in a mechanical shaker. At the end of the experiment, the suspension was filtered through medium paper filters. The filtrate was analyzed for boron concentration by the ICP-OES method. Each sorption experiment was repeated three times in order to have average values. The boron sorption coefficients (the sorption percent, *S* [%], and the sorption capacity, *q* [mg/g]) were calculated from the experimental data in each sample using the following equations:

$$S = \frac{(C_0 - C)}{C_0} \times 100 \quad (1)$$



**Fig. 1.** IR spectra of poly(4-aminostyrene) (a) and poly[4-N,N-bis(2,3-dihydroxypropyl)-aminostyrene] (b).

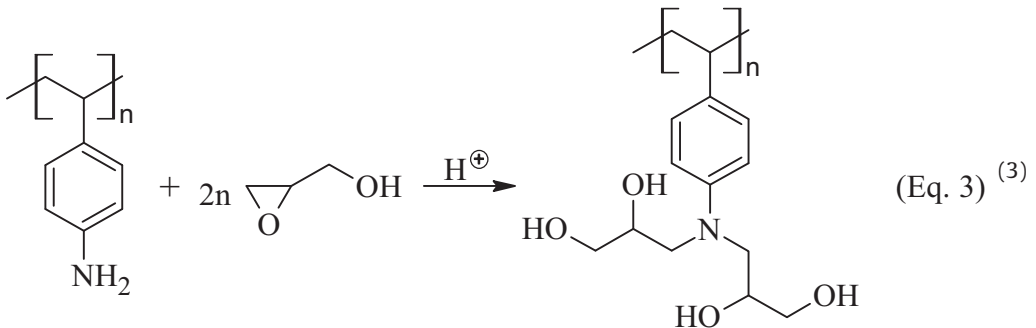
$$q = \frac{(C_0 - C)}{m} \times V_0 \quad (2)$$

where  $C_0$  and  $C$  are the initial and final concentration of boron in the solution [mg/L], respectively,  $V_0$  is the volume of the solution [L] and  $m$  is the mass of the resin [g].

### 3. Results and discussion

#### 3.1. Effect of pH and mechanism of boron sorption

The formation of the GLY-resin films was studied by IR spectroscopy, with a FT-IR spectrophotometer (ATR method). IR spectra of poly(4-aminostyrene) and poly[4-N,N-bis(2,3-dihydroxypropyl)aminostyrene] (GLY-resin) are presented in Fig. 1. In the case of poly(4-aminostyrene), bands at 2924 and 2851 cm<sup>-1</sup> are typical for stretching vibrations of C-H bonds (asymmetrical and symmetrical, respectively). The IR band at 1449 cm<sup>-1</sup> can be assigned to deformation vibrations of C-H bonds (Fig. 1/a). The reaction of poly(4-aminostyrene) with glycidol leads to the formation of structure with many C–O and O–H bonds. Absorption bands (Fig. 1/b) recorded in the region of 3000–3500 cm<sup>-1</sup> (very broad) and 1000–1150 cm<sup>-1</sup> (strong) are characteristic for stretching vibrations of O–H and C–O bonds, respectively. Therefore, the appearance of the abovementioned bands confirms the formation of poly[4-N,N-bis(2,3-dihydroxypropyl)aminostyrene] [26,27]:



The effect of the pH was studied over the pH range 3–10 for an initial boron concentration of 5 mg/L, a shaking time of 24 h, a resin dose of 0.2 g per 25 mL of solution at a temperature of 25 °C. The pH dependence of boron sorption on GLY-resin (Fig. 2) showed that in the acidic medium, boric acid was not bound. With the increasing pH, the sorption capacity of GLY-resin tended to strongly increase up to a maximum at around pH 9.5. These results indicated that borates and hydroxyl groups formed stable complex following the binding of  $B(OH)_4^-$  by the OH groups of organic component that are attached to adjacent carbon atoms in the cis orientation [28].

### 3.2. Sorption isotherms

The study of sorption isotherm is helpful in determining the maximum sorption capacity of sorbate for a given sorbent and in explaining the mechanism of sorption.

The Langmuir, Freundlich and Dubinin – Radushkevich isotherms [29,30] were used to evaluate the boron sorption equilibrium on the GLY-resin. The Langmuir model assumes that the sorption occurs in surface sites where the energy is equal in each size. The Langmuir equation is given by Eq. (4):

$$q = q_m \frac{B \cdot C}{1 + B \cdot C} \quad (4)$$

where  $q_m$  and  $B$  are the Langmuir parameters,  $q_m$  is the sorption capacity [mg/g], expressed as the maximum amount of boron that can be sorbed by the resin as a monolayer and  $B$  is an equilibrium constant that corresponds to the sorption energy [L/mg].

The Freundlich model allows for several kinds of sorption sites in the solid, each having a different energy of sorption. The Freundlich model is usually applied to the sorption processes on heterogeneous surfaces. The Freundlich isotherm is represented by Eq. (5):

$$q = K \cdot C^{1/n} \quad (5)$$

where the parameters  $K$  [mg/g] and  $n$  correspond to the relative sorption capacity and the sorption intensity of the resin, respectively.

Both Langmuir and Freundlich data fitting was done by linearization of Eqs. (4) and (5) as shown by Eqs. (6) and (7), respectively:

$$\frac{1}{q} = \frac{1}{q_m \cdot B \cdot C} + \frac{1}{q_m} \quad (6)$$

$$\log q = \log K + 1/n \log C \quad (7)$$

Plotting  $1/q$  vs.  $1/C$  gives a curve with the slope  $1/(q_m \cdot B)$  and intersection  $1/q_m$ . Plotting  $\log q$  vs.  $\log C$  results in a straight line with the slope  $1/n$  and intersection  $\log K$ .

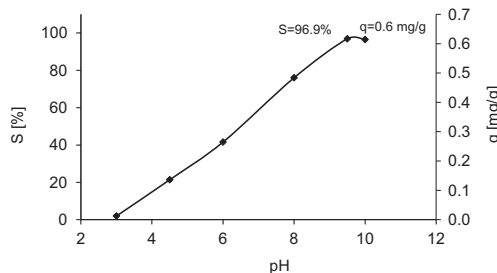


Fig. 2. Sorption of boron on GLY-resin as a function of pH, temperature: 25 °C, sorption time: 24 h, resin dose: 0.2 g/25 mL, initial boron concentration: 5 mg/L.

The essential characteristics of a Langmuir isotherm can be expressed in terms of a separation factor  $R_L$  which is calculated by Eq. (8):

$$R_L = \frac{1}{1+B \cdot C} \quad (8)$$

According to Hall et al. [31], the parameter  $R_L$  indicates the shape of the isotherm  $R_L > 1$ , unfavorable;  $R_L = 1$ , linear;  $0 < R_L < 1$ , favorable; and  $R_L = 0$ , irreversible, respectively. Similarly, the fitness of using the Freundlich equation to describe the sorption can be assessed by the constant  $n$ . If  $1 < n < 10$ , the Freundlich equation is adequate for use [32].

In order to explain the sorption type, equilibrium data was applied to the D-R isotherm. The D-R isotherm is given by the general Eq. (9):

$$q = x_m \exp(-k\varepsilon^2) \quad (9)$$

where  $\varepsilon$  is the Polanyi potential, which is equal to  $RT \ln(1+1/C)$ ,  $x_m$  is the sorption capacity [mg/g],  $k$  is a constant related to the sorption energy [ $\text{mol}^2/\text{kJ}^2$ ],  $T$  is the temperature [K], and  $R$  is the gas constant [kJ/(mol K)]. This expression can be linearized as Eq. (10):

$$\ln q = \ln x_m - k\varepsilon^2 \quad (10)$$

The  $x_m$  and  $k$  values were obtained by plotting  $\ln q$  vs.  $\varepsilon^2$  at a given temperature. The sorption energy (the energy required to transfer 1 mol of sorbate species to the surface of the sorbent from infinity in the bulk of the solution) was obtained from the following Eq. (11):

$$E = -(2k)^{-0.5} \quad (11)$$

If  $E$  is less than 20 kJ/mol, the sorption is the physical in nature due to weak van der Waals forces. The energy for the chemisorption lies in the range 40–800 kJ/mol [33].

Correlation between the equilibrium sorption of boron –  $q_e$  [mg/g] and the equilibrium boron concentration in the solution –  $C_e$  [mg/L] is graphically depicted in Fig. 3. The uptake of boron was studied at a temperature of 25 °C, and pH=9.5, and in the boron concentration range of 4–30 mg/L while the dose of GLY-resin was held constant at 8 g/L and sorption time of 24 h. The sorption isotherm, as shown in Fig. 3 was regular, positive and convex to the concentration axis for GLY-resin. Sorption percent  $S$  and capacity  $q$  were high and equaled 98.5% for low initial concentration of boron and 1.6 mg/g for concentration of 30 mg B/L, respectively.

Linearly transformed Langmuir, Freundlich and D-R isotherms were fitted to the experimental data (Fig. 4). The parameters obtained from the linear fits appropriately and the correlation coefficients are presented in Table 1. It was found that the experimental data satisfies the Langmuir model providing a good correlation of the experimental equilibrium data ( $R^2=0.9771$ ). The calculated Langmuir parameters were:  $q_m=1.2614$  mg/g and  $B=7.8263$  L/mg at 25 °C. Rather good applicability of the

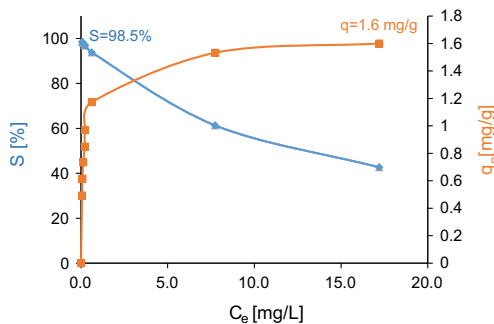


Fig. 3. Isotherms of boron sorption on GLY-resin at temperature of 25 °C, pH=9.5, resin dose: 0.2 g/25 mL, initial boron concentration: 4–30 mg/L, sorption time: 24 h.

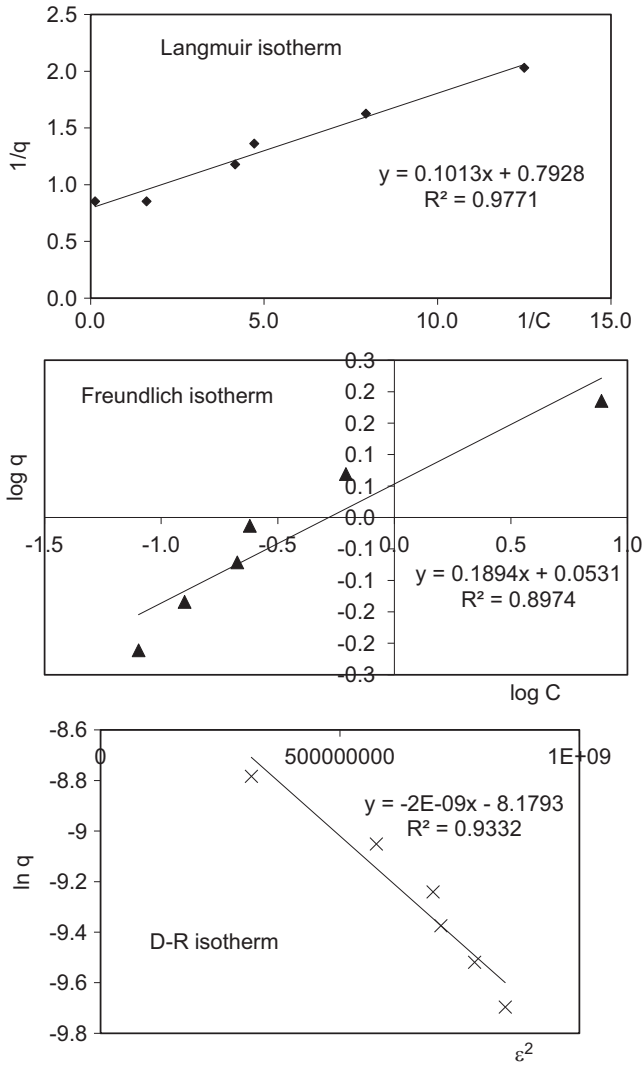


Fig. 4. Langmuir, Freundlich and D-R isotherms at temperature of 25 °C, pH=9.5.

Table 1

Parameters of Langmuir, Freundlich and Dubinin-Radushkevich isotherms for GLY-resin at 25 °C, pH=9.5.

Langmuir parameters					Freundlich parameters			Dubinin-Radushkevich parameters						
R <sup>2</sup>	q <sub>m</sub> [mg/g]	B [L/mg]	R <sub>L</sub> for C <sub>0</sub> [mg/L]					R <sup>2</sup>	K [mg/g]	n	R <sup>2</sup>	X <sub>m</sub> [mg/g]	k [mol <sup>2</sup> /J <sup>2</sup> ]	E [kJ/mol]
			5	7	8	10	20							
0.9771	1.2614	7.8263	0.025	0.013	0.006	0.004	0.003	0.8974	1.061	5.345	0.9332	2.804	1E-09	15.81

Langmuir isotherm can suggest the L type of isotherm according to the Giles et al.'s classification [34]. The calculated equilibrium parameters R<sub>L</sub> (listed in the Table 1) in the range of 0 – 1, indicate favorable sorption for boron on GLY-resin in the studied range of initial boron concentration.

The Freundlich and the Dubinin – Radushkevich models are less suitable than the Langmuir model for the representation of the sorption data, as reflected by lower correlation coefficients ( $R^2$ ), obtained from the linear fits of the data in all cases. Very good applicability of the Langmuir isotherm at 25 °C suggests the monolayer coverage of the borate onto GLY-resin.

As it can be seen in Fig. 3, the amount of sorbed boron increases steady with concentration until the surface sites are saturated with a sorbate and no further process occurs. This behavior indicates that the isotherm can be classified as L type. Furthermore, the sorption of boron on the resin was rapid and increased even at high concentrations which supports the L type of isotherm (or I type according to YUPAC classification).

### 3.3. Effect of sorption time

The effect of time on the boron sorption was studied using 0.2 g of GLY-resin beads per 25 mL of solution and an initial boron concentration of 5 mg/L at the pH=9.5, temperature of 25 °C and shaking time from 2 to 24 h. The variation of the boron sorption as a function of time is shown in Fig. 5.

The maximum boron sorption (ca. 96%) was reached after 12 h and increased insignificant to 24 h. In order to explain the mechanism involved in the sorption process the Lagergren pseudo-first and pseudo-second-order and the Elovich equation and the parabolic diffusion model were used [30,35]. The pseudo-first-order model is given by the Eq. (12):

$$\log(q_e - q_t) = \log q_e - k_1 t / 2.303 \quad (12)$$

where  $q_t$  and  $q_e$  are the amounts of boron sorbed [mg/g] at any time  $t$  and at the equilibrium time, respectively, and  $k_1$  is the pseudo-first-order rate constant for the sorption process [1/h].

The pseudo-second-order kinetics is expressed by the Eq. (13):

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (13)$$

where  $k_2$  is the pseudo-second-order rate constant [g/(mg h)].

The overall kinetics of the sorption from solutions may be governed by the diffusional processes as well as by the kinetics of the surface chemical reaction. In diffusion studies, the rate is often expressed in terms of the square root time (Eq. (14)):

$$q_t = k_p t^{1/2} \quad (14)$$

where  $k_p$  is the intraparticle diffusion rate constant [mg/(g(h)<sup>1/2</sup>)]

The plots of  $\log(q_e - q_t)$  vs.  $t$ ,  $t/q_t$  vs.  $t$  and  $q_t$  vs.  $t^{1/2}$  obtained from above models checked statistically and graphically should be a straight line with the slope  $-k_1/2.303$  and intersection  $\log q_e$ , the slope  $1/q_e$  and intersection  $1/k_2 q_e^2$  respectively, and  $k_p$  as a slope of the plot of  $q_t$  vs.  $t^{1/2}$  if the sorption process fits to the related equation. Moreover constant  $k_2$  is used to calculate the initial sorption rate at  $t=0$ ,  $r$ , which is defined by Eq. (15):

$$r = k_2 q_e^2 \quad (15)$$

where  $r$  is the initial sorption rate [mg/(g h)].

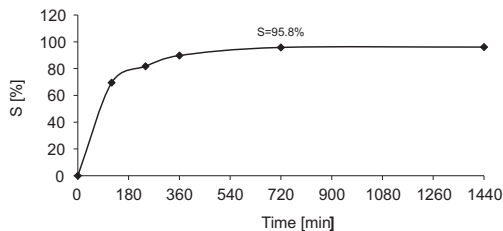


Fig. 5. Kinetics of boron sorption on GLY-resin at temperature of 25 °C, pH=9.5, resin dose: 0.2 g/25 mL, initial boron concentration: 5 mg/L.



The resulting parameters of these models calculated and the correlation coefficients  $R^2$  are listed in Table 2, where the experimental value of  $q_e$  is also presented. The results show that the intraparticle diffusion model was not applicable for the presented process due to the lower correlation coefficients. However, for the pseudo-first-order rate kinetic model, the coefficient  $R_1^2$  was 0.9898, the calculated value  $q_1=0.537$  mg/g did not agree with the experimental one (0.600 mg/g). The pseudo-second-order model expression provided the appropriate correlation with the experimental data. The high value of the  $R_2^2=0.9996$  and the good agreement between the calculated and the experimental values of  $q_e$  in this model demonstrate that the pseudo-second-order model adequately describes the boron sorption on GLY-resin.

### 3.4. Effect of temperature

The effect of temperature on the sorption of boron on GLY-resin was tested out at pH 9.5 and a temperature of 20, 30, 40, 50 and 60 °C for an initial boron concentration of 5 mg/L, a shaking time of 24 h and a resin dose of 0.2 g per 25 mL. In order to understand the effect of temperature on the sorption process thermodynamic parameters ( $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ ) were calculated [36]. The molar free energy change of the sorption process is related to the equilibrium constant ( $K_c$ ) and calculated from the Eq. (16):

$$\Delta G^\circ = -RT \ln K_c \quad (16)$$

where  $R$  is the gas constant (8.314 J/(mol K)) and  $T$  is the temperature [K]. The  $K_c$  values were estimated as (Eq. (17)):

$$K_c = (C_0 - C)/C \quad (17)$$

Each  $K_c$  value was the average of all experimental values ( $C_0$  and  $C$ ) obtained at constant temperature that the sorption experiments were carried on.

Standard enthalpy change,  $\Delta t_a$ , and the standard entropy change,  $\Delta a$ , of sorption can be calculated by using the following equation (Eq. (18)):

$$\ln K_c = -\Delta H^\circ / RT + \Delta S^\circ / R \quad (18)$$

Plotting  $\ln K_c$  vs.  $1/T$  produces a straight line with the slope  $-\Delta H^\circ/R$  and intersection  $\Delta S^\circ/R$ .

Standard entropy and enthalpy changes of the sorption of boron on GLY-resin were calculated as,  $\Delta S^\circ=0.15$  kJ/(mol·K) and  $\Delta H^\circ=-39.36$  kJ/mol, respectively (Table 3). The positive value of  $\Delta S^\circ$

**Table 2**

Kinetic parameters for boron sorption on GLY-resin at 25 °C, initial boron concentration 5 mg/L, resin dose 0.2 g/25 mL, pH=9.5.

Model of sorption kinetics	Parameters of kinetic models			
Pseudo-first-order	$q_1$ [mg/g]	$k_1$ [1/h]	$R_1^2$	
	0.537	0.00783	0.9898	
Pseudo-second-order $q_e(\text{expt.})=0.600$ mg/g	$q_2$ [mg/g]	$k_2$ [g/(mg h)]	$R_2^2$	$r$ [mg/(g h)]
	0.622	0.035585	0.9996	
Diffusion model	$C$ [mg/g]	$k_p$ [mg/(g·(h) <sup>1/2</sup> )]	$R_p^2$	
	0.006	0.4167	0.7316	

**Table 3**

Thermodynamic parameters of boron sorption on GLY-resin at different temperatures.

Temp. [°C]	$S$ [%]	$K_c$	$\Delta G^\circ$ [kJ/mol]	$\Delta H^\circ$ [kJ/mol]	$\Delta S^\circ$ [kJ/(mol K)]
20	82.64	4.76	-3.80		
30	91.39	10.61	-5.95		
40	93.00	13.29	-6.73	39.36	0.15
50	93.69	14.85	-7.24		
60	94.33	16.64	-7.78		

showed the increased randomness at the solid-solution interface during the sorption. The positive value of  $\Delta H^\circ$  indicated that the boron sorption is the endothermic process. As it can be seen in Table 3, boron sorption and  $K_c$  (equilibrium constant) values increased with an increase of temperature. In contrast, the  $\Delta G^\circ$  values decreased when the temperature increased. The negative values of  $\Delta G^\circ$  at the range 20–60 °C implied that the sorption of boron on GLY-resin was spontaneous. The positive  $\Delta S^\circ$  value corresponds to an increase in the degree of freedom of the sorbed species. In addition to this, as the values of  $\Delta G^\circ$  decreased with an increase of temperature, the spontaneous nature of sorption is directly proportional to the temperature.

### 3.5. Effect of resin dosage

To investigate the effect of resin dosage on boron sorption, the concentration of GLY-resin was varied from 2 to 12 g/L at 25 °C while the initial concentration of boron, pH and time were held constant at 5 mg/L, 9.5 and 24 h, respectively.

The sorption of boron increased with an increase in the GLY-resin dose (Fig. 6) which can be attributed to the availability of more sorption sites – hydroxyl groups and contributed to the chemical nature of the process. The sorption of boron of ca. 99% was obtained for the GLY-resin dose of 0.2 g per 25 mL of solution (8 g/L). There was no significant change in the boron removal for higher doses of resin.

### 3.6. Desorption tests

HCl (2 mol/L) solution was used as eluent for desorbing boron from GLY-resin (poly[4-*N,N*-bis(2,3-dihydroxypropyl)aminostyrene]). Furthermore, to determine the reusability of GLY-resin, sorption–desorption cycles were repeated twice. The quantitative desorption yield in first and second cycle was confirmed. Sorption-desorption efficiency,  $E_{S-D}$  [%], was calculated using the following relationship:

$$E_{S-D} = \frac{q_{n+1}}{q_n} \times 100 \quad (19)$$

where  $q_n$  is the total sorption capacity in the first cycle and  $q_{n+1}$  is the total sorption capacity in the next cycle [mg/g]. The result of 100% sorption-desorption efficiency, means that no decrease in the boron sorption occurred in the 2nd cycle.

### 3.7. Boron removal from post-crystallization lye

The latest experiment tested the boron uptake by GLY-resin from real medium having a boron concentration of 9.09 mg/L. Post-crystallization lye (25 mL) was contacted with various amounts of GLY-resin beads for 24 h at 25 °C under pH ca. 9.5.

The sorption isotherm is shown in Fig. 6 and it is regular, positive and convex to the concentration axis for GLY-resin. As seen in Fig. 6, boron uptake increased with an increase in the amount of

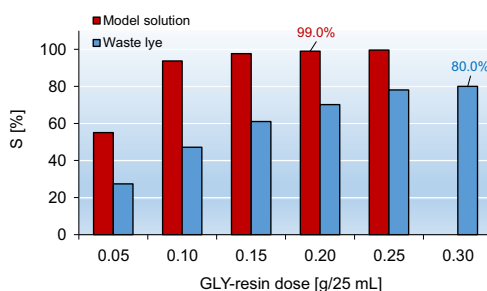


Fig. 6. Sorption of boron as a function of GLY-resin dose, temperature: 25 °C, pH=9.5, sorption time: 24 h, initial boron concentration: 5 mg/L-model solution, 9.1 mg/L-post-crystallization lye.

GLY-resin beads dozed into the waste lye. The boron removal was 80.0% with 10 g resin/L-post-crystallization lye. The boron sorption from waste lye is weaker than from the model solution, however, the initial concentration of boron is higher almost twice.

#### 4. Conclusions

A new polystyrene-based resin containing vicinal hydroxyl groups (GLY-resin) was synthesized to determine its sorption properties toward boron compounds. The experimental results showed that the GLY-resin had a higher affinity to boron than precursor (product of Purolite A170). Furthermore, pH and temperature of boron solution, resin dosage and contact time affected the boron sorption by GLY-resin. It was found as follows:

- The sorption of boron had a maximum around pH=9.5 in the pH range 3–10.
- The thermodynamic experiments proved that boron sorption increased with an increase in temperature of the solution ( $\Delta H^\circ > 0$ ). The calculated value of  $\Delta G^\circ < 0$  showed the spontaneous sorption of boron on GLY-resin in the investigated temperature range of 20–60 °C.
- The kinetic study revealed that the pseudo-second-order mechanism was the rate determining step boron sorption on GLY-resin. Optimum time of sorption was determined as 24 h.
- Boron sorption increased with an increase of resin dose, which is due to the rise in surface area. A meaningful increase took place up to 8 g/L–model solution and 10 g/L-post-crystallization lye.
- The Langmuir isotherm fitted better the experimental data than the Freundlich and D-R models. It proves the homogeneous nature of boron sorption on synthesized GLY-resin. The sorption energy value calculated as 39 kJ/mol, which corresponds to chemisorption.
- The maximum sorption capacity was 1.6 mg/g, while the maximum removal achieved was 98.5% at 5 mg/L feed B conc.
- Purolite A170 grafted with glycidol can be an alternative resin to beads containing NMDG functional groups for removal of boron dissolved in water.
- New boron bonding GLY-resin seems to be promising for practical uses, due to its easy regeneration with 2 M HCl and unchanged boron sorption capacities after recycling.

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