Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS

J. Serb. Chem. Soc. 83 (2) 251–264 (2018)
JSCS–5072

UDC 547.27+541.183+547.914:54–145.2:
544.351:544.43
Original scientific paper

Boron removal from aqueous solutions by a polyethylenimine–epichlorohydrin resin

SOFIA SARRI[1], PANAGIOTIS MISAELIDES[1]*, DIMITRIOS ZAMBOULIS[1]
and JOLANTA WARCHOŁ[2]

[1]Department of Chemistry, Aristotle University of Thessaloniki, GR-54124 Thessaloniki, Greece and [2]Department of Water Purification and Protection, Rzeszow University of Technology, Rzeszow, Poland

(Received 4 July, revised 25 September, accepted 30 October 2017)

Abstract: The use of a polyethylenimine–epichlorohydrin resin for the boron removal from aqueous solutions (boron concentration: 100–5000 mg L^{-1}) of non-adjusted and pre-adjusted pH (pH_{nat}, pH_{init} 8.0, 9.0 and 10.0) aqueous solutions was investigated using a batch technique. The boron concentration in the solutions after sorption was determined photometrically. The results indicated that the pH-dependent boron uptake was related to the protonation/deprotonation of the surface functional groups of the resin and to the boron speciation in solutions of different pH values. The maximum boron sorption capacity observed in solutions of pH 9.0 was 55 mg g^{-1} exceeding the majority of other commercial or alternative sorbents. Five empirical adsorption equations (Freundlich, Langmuir, Redlich–Peterson, Langmuir–Freundlich and Toth) were applied to the modelling of the boron adsorption equilibrium. The modelling results identified the homogenous boron sorption from acidic and heterogeneous from alkaline solutions. At alkaline pH, the system non-ideality can originate either from the different binding mechanism or from the competitive sorption of different boron species. The homogenous type boron sorption from acidic solutions was further confirmed by kinetic studies.

Keywords: boron removal; polyethylenimine–epichlorohydrin resin; sorption equilibrium; kinetics; modeling.

INTRODUCTION

Boron occurs in a number of minerals (*e.g.*, kernite, borax, ulexite, colemanite) mainly combined with oxygen and can be released into air, water or soil, as a consequence of natural weathering of soils or rocks. The average boron concentration in Earth's crust is approximately 0.0008 %. Boron can also be found in the environment as a result of human activities, since borate-containing

---

* Corresponding author. E-mail: misailid@chem.auth.gr
https://doi.org/10.2298/JSC170704114S

minerals are mined and processed to produce borates for several industrial applications (*e.g.*, production of glass and ceramics, soaps and detergents, fire retardants, agricultural fertilizers and pesticides, water treatment chemicals and fuel additives). Smaller amounts of boron can additionally be released to the environment by coal-burning power plants and copper smelters.[1]

Boron is an essential element and micronutrient for plants but its essentiality for humans has not yet been convincingly demonstrated. However, the regular use of irrigation waters with boron concentrations higher than 1 mg L^{-1} can be harmful for many plants.

Animal oral exposure studies have clearly identified the reproductive system and developing fetus as the most sensitive targets of boron toxicity, while case reports with humans indicated that the liver and kidneys are also susceptible to high dose levels.[1,2] The boron toxicology was intensively studied and a tolerable upper intake level (UL) for humans of 0.16 mg kg^{-1} by day^{-1} (10 mg per adult) was obtained by the European Food Safety Authority (EFSA) from the comprehensive reproductive toxicity studies.[3,4]

The boron content in drinking, irrigation and wastewater is mostly regulated by the legislation of the individual countries. The suggested limits are not common and considerably differ among different countries. The World Health Organization (WHO) Drinking-water Quality Committee revised the previous boron guideline value to 2.4 mg L^{-1}.[4] On the other hand, the EFSA, in order to protect all age groups, suggested that the natural mineral waters should contain no more than 1.5 mg L^{-1} of boron.[5]

The boron removal from aqueous media is not simple. Several separation technologies, such as adsorption by inorganic and organic sorbents,[6–10] ion exchange,[6–9,11–16] solvent extraction[15,17] and reverse osmosis,[18,19] have been proposed and applied for recovering boron from aqueous solutions. In the literature there are also reviews on the methods proposed for the boron removal from aqueous media[20] and on the technologies for boron removal from saline waters and seawater.[21,22] As indicated in the literature, there is no evidence that boron compounds could significantly be removed by coagulation/flocculation, sedimentation, and inert media filtration. Therefore, ion-exchange and reverse osmosis could be considered as the most appropriate techniques for the boron removal from aqueous media. The use of hydroxyl-containing synthetic resins for this purpose was also found to be especially promising.[19,23,24]

In the present study the ability of a polyethylenimine–epichlorohydrin resin (PEI) to remove boron from aqueous media was investigated under various conditions. This resin molecules possess amino- and amide-groups, capable to chelate the cationic and adsorb, through electrostatic interactions or hydrogen bonding, the anionic species. The obtained data were used for modelling of the adsorption behaviour of the resin using empirical equilibrium and kinetics equations.

The sorption ability of the material was also compared with the literature data for other sorbents.

EXPERIMENTAL

In the present study a polyethylenimine–epichlorohydrin resin was prepared and used as boron sorbent. The resin was prepared using a low-molecular weight polyethylenimine (M.W. ~2000) and a modification of a previously described synthetic method.[25] The main modifications of the resin synthesis consisted in the selection of a lower preparation temperature (60 °C) and the use of Igepal BC/6 (nonylphenol ethoxylate) as a surfactant.

The boron sorption experiments were performed using a batch technique. Boron solutions of initial concentration (c_{init}) between 100 and 5000 mg L^{-1} were prepared by dissolution of H_3BO_3 solution (Panreac) with bi-distilled water. The initial pH (pH$_{\text{init}}$) of the solutions was adjusted to 8.0, 9.0 and 10.0 respectively, using a dilute NaOH solution. For comparison purposes the boron sorption behaviour of the resin was also investigated in boric acid solutions of non-adjusted pH (pH$_{\text{nat}}$). The pH of the last solutions was between 3.3 and 5.6, depending on the boron concentration. The preliminary boron sorption experiments in the presence of competing Cl^- and SO_4^{2-} were also performed. For the sorption experiments 50 mg of the resin were shaken for 24 h with 10 mL of the boron solutions in closed 15 mL polyethylene terephthalate (PET) tubes (supplied by Corning Inc.) under ambient conditions (t = = 25 °C). At the end of the contact time and the separation of the solid from the liquid phase, the boron concentration of the solution was determined photometrically using carmine as colour forming agent at 585 nm.[26] The data obtained were used to calculate the corresponding boron uptake, mg g^{-1}, values:

$$q_{\text{e}} = \frac{c_{\text{init}} - c_{\text{e}}}{M} V \tag{1}$$

where c_{init} and c_{e} are the initial and equilibrium boron concentration in the liquid phase, mg L^{-1}, respectively, M is the mass of adsorbent in g and V is the volume of the solution in L.

Sorption kinetics experiments were conducted to determine the equilibration time using the boron solutions of non-adjusted pH (c_{init}: 250, 500 and 1000 mg L^{-1}). At the specific time intervals the boron concentration in small volumes of the solution, not considerably affecting the solid to liquid ratio, was determined using the previously mentioned analytical technique.

RESULTS AND DISCUSSION

The expected chemical structure of the resin, along with a plausible reaction scheme, is presented in Fig. 1. Arrows indicate the possible reaction sites with epichlorohydrine during the second step of the synthesis. An interaction example is also given in the same figure. Epichlorohydrine was mainly used during the second synthesis step as a cross-linker to transform a water soluble polyamine into an insoluble resin. The cross-linking also created the additional quaternary amino-groups.

The resin particles were spherical with an average diameter of *ca.* 100 µm (Fig. 2). The resin was not crystalline and had a specific surface area of 0.575 m^2 g^{-1}. The scanning electron microscope (SEM) examination of the resin particles using a JEOL JSM 840A equipment revealed the indentations of various dimensions on their surface.

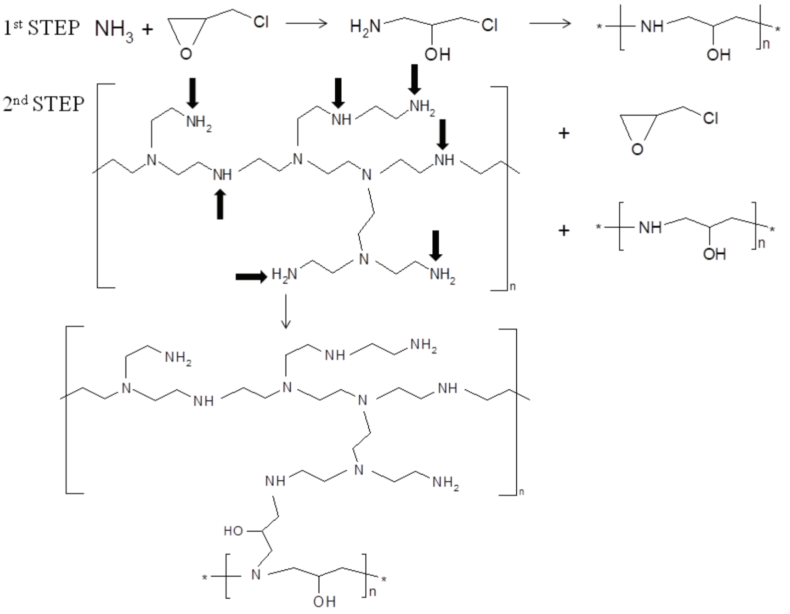

Fig. 1. Expected chemical structure of the resin and a plausible reaction scheme. Arrows indicate the possible reaction sites with epichlorohydrine during the second step of the synthesis.

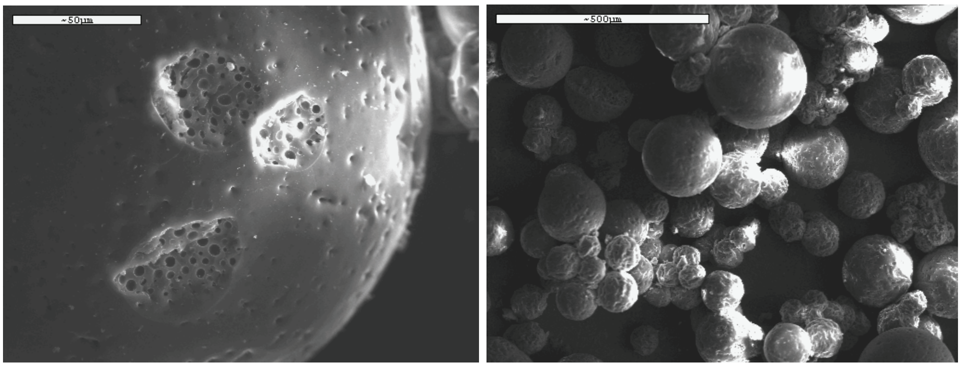

Fig. 2. SEM images of the resin particles of different size showing indentations on their external surface.

The X-ray photoelectron spectroscopic (XPS) analysis of the resin, performed using monochromatic Al X-rays, supplied by VG Scientia MX-650 source at the Chemistry Faculty of UCLM Lublin, showed the existence of both tertiary and quaternary amino-groups (N1s binding energies of 399 and 401.5 eV).[27–29] The quaternary amine groups can exchange anions in a very wide pH range due to their permanent positive charge, whereas tertiary amines can only exchange anions in the pH-range where they are protonated.

The XPS spectra before and after the boron sorption are presented in Fig. 3. In the XPS spectrum after the sorption a peak at 192 eV indicates the presence of boron. This binding energy could be assigned to boron bonding with oxygen and nitrogen.

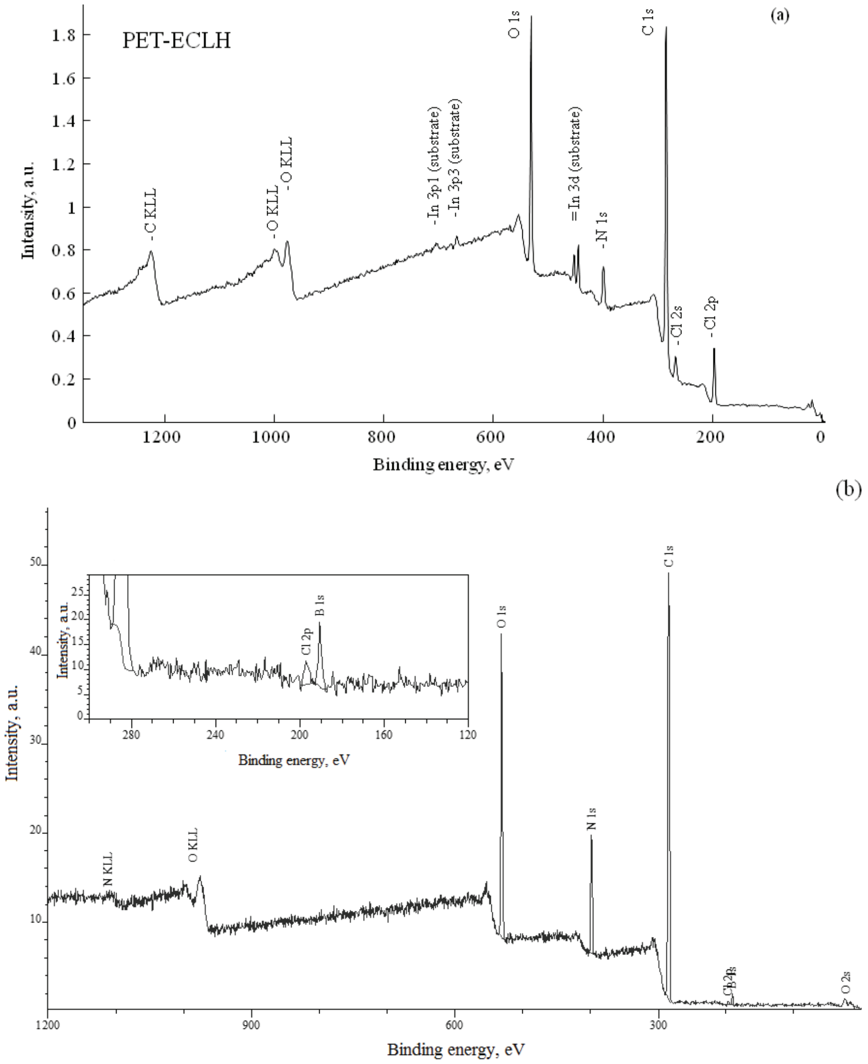

Fig. 3. XPS Spectrum before (a) and after (b) boron sorption.

The sorption isotherms of the resin are given in Fig. 4. The variation of the equilibrium pH (pH_e) of the solutions as a function of their initial boron concentration (c_{init}) is also presented in the same figure. The experimental maximum sorption capacity of the resin (denoted as $q_{m,exp}$) is given in Table I.

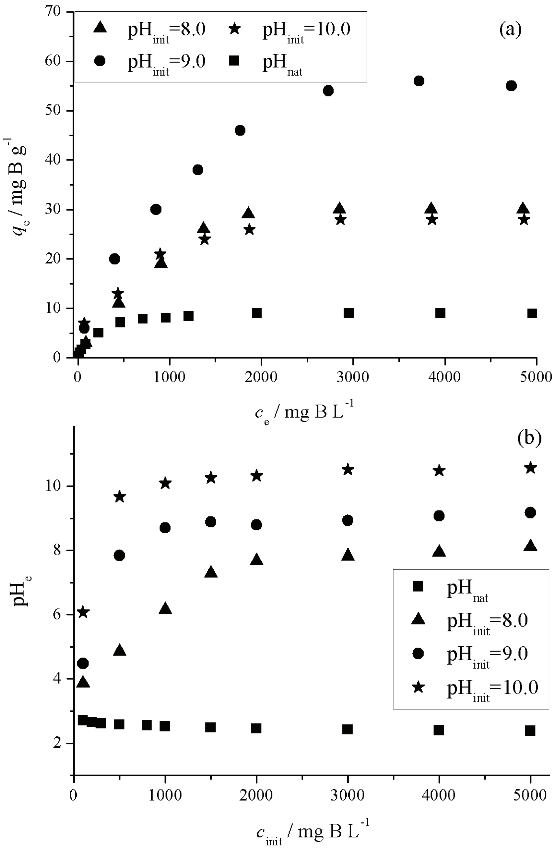

Fig. 4. Equilibrium isotherms for the boron sorption (a) and the pH_e of boron solutions (b).

TABLE I. Experimental maximum boron sorption capacity, $q_{m,exp}$, of the resin

pH	$q_{m,exp}$ / mg g^{-1}
pH_{nat} (3.3 – 5.6)	9
Pre-adj. pH 8.0	30
Pre-adj. pH 9.0	55
Pre-adj. pH 10.0	28

The resin showed high uptake values in basic environments drastically decreasing under acidic conditions. This could likely be ascribed to the boron speciation in the aqueous solutions as well as to the surface functional groups of the resin.

Under the acidic conditions (s. pH_{nat}), the tertiary amine functional groups become protonated, resulting in the positively charged surfaces of the sorbent: $R_3N + H^+ \leftrightarrows R_3NH^+$. As illustrated in Fig. 4, the boron uptake capacity from solutions of pH_{nat} (pH_e *ca.* 3.0) is much lower than the corresponding one from the alkaline solutions (pH 8.0–10.0). According to the speciation diagrams, calculated using the chemical equilibrium program Visual MINTEQ ver. 2.53 (Fig. 5), the predominant boron species in acidic solutions is the neutral boric acid. Its removal by the resin could occur via the coordination to non-protonated amino-groups. Nevertheless, the pH_e variation (Fig. 4) for solutions of pH_{nat} is insignificant over the whole boron concentration range, indicating that all hydrogen cations were consumed in the amino-group protonation process becoming unavailable to the neutral boric acid.

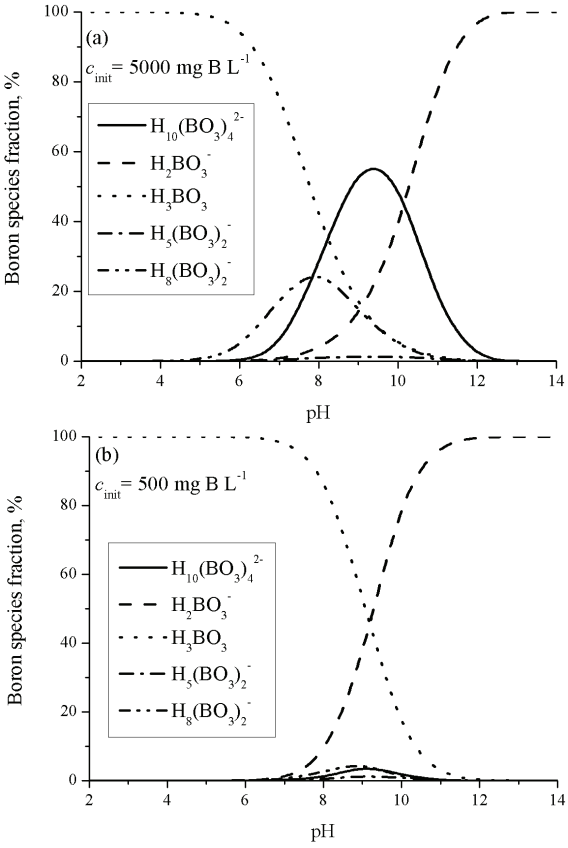

Fig. 5. Fraction diagrams of boron species in solutions of varying pH (c_{init} = 5000 mg L^{-1} (a); c_{init} = 500 mg L^{-1} (b)).

Under alkaline conditions (pre-adj. pH 8.0–10.0), the boric acid is hydrolyzed. The released proton is retained by the tertiary amine sites behaving as a weak basic anion exchanger.[16] However, in the view of the efficient sorption of boron by the resin from alkaline solutions, the presence of an additional sorption mechanism cannot be excluded. As shown in Fig. 5, when the pH increases from 8.0 to 9.5, the percentage of boric acid decreases from *ca.* 35 to 25 %, and to 0 % at pH > 10.5. In every case, the bonded boron is coordinated by at least one amine-group. Accordingly, the stoichiometric amount of hydrogen cations is released from the sorption surface. Their presence in the solution is confirmed by the decrease of pH_e ($pH_e <$ pre-adj. pH, Fig. 4).

As the boron initial concentration rises, the pH_e of the solutions approaches the pre-adjusted one. Hydrogen cations can react with either the hydroxyl groups or with an "excess" of boron salt present in the solution: $2H_2BO_3^- + 2H^+ \rightleftarrows$ $\rightleftarrows H_5(BO_3)_2^-$. The enhanced boron uptake from solutions of pH 9.0 could be thermodynamically explained taking into account the boron speciation and the ratio charge of the complex to the number of boron atoms. In solutions of pH 9.0, the divalent anion $H_{10}(BO_3)_4^{2-}$ is the predominant species, while in those of pH 8.0 and 10.0 the ratio of bivalent/monovalent anions is close to unity (Fig. 5). The high affinity of polyethylenimine–epichlorohydrin resins for bivalent ions was also previously observed in the case of uranium sorption.[30] On the other hand, the high pH values are related to the increased hydroxyl-ion concentration in the solution, which may have certain affinity to the positively charged surface as well. The increased competition for the active sites in solutions of pH 10.0 consequently leads to a reduction of the boron sorption.

The bonding of boron with nitrogen was also observed in the XPS data obtained for the boron-loaded resin. These data indicate that the majority of the boron in the resin is bound with nitrogen and oxygen.

The sorption experiments in the presence of chlorides and sulphates showed that both of them reduced the boron uptake. The uptake was lower in the case of sulphates, most probably due to higher stereochemical hindrance and charge.

The experimental data were used for modelling calculations. The equilibrium isotherm data were fitted using the two-parameter Langmuir (L) and the Freundlich (F) and the three-parameter Redlich–Peterson (R–P), the Langmuir–Freundlich (L–F) and the Toth (T) equations (Table II). The Langmuir model assumes a localized monolayer adsorption on a fixed number of adsorption sites of equal energy (homogenous sorption). In contrast, the Freundlich model con-

TABLE II. Equilibrium equations used for the modeling of the experimental data; q_e and c_e are equilibrium boron concentrations in the solid (in mg g^{-1}) and liquid (in mg L^{-1}) phase, respectively, q_m the maximum sorption capacity (in mg g^{-1}), K the equilibrium constant and n *a* parameter characterizing the system heterogeneity

Isotherm model	Equation
Langmuir (L)	$q_e = q_m K_L c_e / 1 + K_L c_e$
Freundlich (F)	$q_e = K_F c_e^{1/n}$
Redlich–Peterson (R–P)	$q_e = q_m K_{RP} c_e \Big/ 1 + \left(K_{RP} c_e\right)^n$
Langmuir–Freundlich (L–F)	$q_e = q_m \left(K_{LF} c_e\right)^n \Big/ 1 + \left(K_{LF} c_e\right)^n$
Toth (T)	$q_e = q_m K_T c_e \bigg/ \left[1 + \left(K_T c_e\right)^n\right]^{1/n}$

siders the surface heterogeneity and does not reach a limited sorption capacity. The applied three-parameter models combine elements of both Langmuir and Freundlich equations, assuming the heterogeneous adsorption on a surface with limited amount of adsorption sites. Hybrid equations incorporate an additional parameter – the surface heterogeneity factor (n) which, if equals unity, reduces the three-parameter models to the Langmuir equation, applicable for monolayer coverage of an ideal surface.

The non-linear curve fitting was carried out using the Levenberg–Marquardt algorithm. The isotherm parameters were determined by minimizing the sum of the squares of the errors (objective function), across the concentration range studied. To make the iteration procedure well-posed, similar to the previous study, the experimentally obtained value of the maximum adsorption capacity ($q_{\mathrm{m,exp}}$) was used as initial guess for the estimation of q_{m}.[31] The relationship between the two variables (experimental and theoretically predicted) was assessed by the approximation of standard deviation (σ), the Fisher test (F) and the mean error (ME in %).

Fig. S-1a–d of the Supplementary material to this paper compares the experimental isotherm data obtained for boron sorption and the curves calculated using the applied equilibrium model equations. The best criteria value of statistical tests for the Langmuir model was obtained for data set at $\mathrm{pH_{nat}}$ ($\mathrm{pH_e} \sim 3.0$, Table S-I of the Supplementary material). However, it did not reflect the best approximation of the experimentally obtained maximum sorption capacity value ($q_{\mathrm{m,exp}}$). In alkaline pH the three-parameter models are more adequate than the Langmuir one, to describe the sorption process. The estimated value of parameter $n \neq 1$ further confirmed the system heterogeneity, that could stem from both the different mechanisms of the B(III) sorption and the different affinity of the resin for mono- and bi-valent boron species. Nevertheless, the results of statistical tests do not clearly identify which of the three-parameter models is the best one. The visual examination of modelling curves and the statistical test results indicate that the Freundlich equation gave the worst fit to all experimental data sets. However, it is clearly evident that the extent of the Freundlich model discrepancy is lower in alkaline pH (heterogeneous sorption) than in acidic one (homogenous sorption).

Fig. S-2 of the Supplementary material illustrates the experimental data of the sorption kinetics along with the modelling results. It is obvious that in the first 2 min *ca.* 75 % of the boron could be removed from the solutions. The removal efficiency increases with the time at all studied initial concentrations (250, 500 and 1000 mg $\mathrm{L^{-1}}$) and reaches the equilibrium within several minutes. The sorption process was modelled using five surface reaction models describing the rate of variation of the boron concentration in the liquid phase (1st and 2nd order irreversible or reversible and adsorption).[32]

The irreversible reaction models assumed irreversible interaction between boron and binding sites on the resin surface. The detailed kinetic considerations are given in Supplementary material.

The kinetic constants and the statistical tests results are given in Table III.

Table III. Constants of the kinetic models for the boron sorption by the PEI resin from solutions of different c_{init} at $\mathrm{pH_{nat}}$ (σ: standard deviation, F: the Fisher test and ME, % the percent mean error)

Model	k	σ	F	ME, %
	c_{init} = 250 mg L^{-1}			
1st order irreversible	2.05×10^{-6}	21.26	0.02	8.61
1st order reversible	5.57×10^{-4}	2.18	2.06	0.80
2nd order irreversible	1.01×10^{-8}	21.14	0.02	8.61
2nd order reversible	1.78×10^{-6}	2.40	1.57	0.86
Adsorption	1.35×10^{-5}	1.32	5.22	0.42
	c_{init} = 500 mg L^{-1}			
1st order irreversible	2.78×10^{-6}	25.64	0.09	5.03
1st order reversible	3.43×10^{-4}	3.92	4.20	0.60
2nd order irreversible	1.44×10^{-8}	33.41	0.05	5.77
2nd order reversible	6.00×10^{-7}	4.55	2.86	0.70
Adsorption	8.40×10^{-6}	3.15	5.94	0.35
	c_{init} = 1000 mg L^{-1}			
1st order irreversible	6.44×10^{-7}	28.71	0.05	2.65
1st order reversible	1.66×10^{-4}	4.90	1.80	0.38
2nd order irreversible	1.09×10^{-8}	199.41	0.00	11.59
2nd order reversible	2.40×10^{-7}	6.71	0.85	0.49
Adsorption	3.65×10^{-6}	4.79	1.68	0.36

The concentration decay curves calculated by the kinetics models (lines) are given in Fig. S-2a–c in comparison with the three experimental data sets (symbols). The visual examination of Fig. S-2 as well as the analysis of the results of the statistical tests, depicted in Table III, clearly show that neither the 1st nor the 2nd order irreversible model successfully reproduce the experimental data. This suggests a reversible reaction of boron binding to resin surface. Furthermore, the better approximation obtained for the 1st order reversible model than for the 2nd order one indicate the lack of sorbate–sorbate interaction, thus supporting a monolayer surface coverage.[33] The lowest values of both the approximation of standard deviation and the mean error, as well as the highest value of the Fisher test show that, among the applied models, the best fit was obtained using the adsorption one. It further confirmed a homogenous boron sorption on the resin at $\mathrm{pH_{nat}}$. The observed deviation of the curves obtained by the experimental points (Fig. S-2b) could be due to the fact that the value of maximum adsorption capacity (q_{m}) used in this model, was not experimentally obtained, but estimated from the equilibrium Langmuir equation (q_{m} = 9.59 mg g^{-1}, see Table S-I). It is generally difficult to distinguish among kinetic models on the basis on how well they fit the experimental data, as the models based on different assumptions (*e.g.*, the 1st order reversible and the adsorption) can often provide nearly identical fits (*e.g.*, s. experimental set for c_{init} 1000 mg L^{-1} in Fig. S-2c). Nevertheless, as can be seen from Table III, the boron binding in low concentration solutions (c_{init}) results in higher constant (k) values for either the adsorption model or the 1st reversible kinetics model, reflecting fast reaction kinetics. The observed dependence of the surface interaction rate constants (k) on c_{init} may be attributed to the degree of boron loading on the adsorbent surface.[34]

The experimental results obtained from the investigation of the synthesized polyethylenimine–epichlorohydrin resin indicated its suitability as potential sorbent for the removal of boron anionic species from aqueous media. As shown in Table IV its sorption capacity is significantly higher than that of the majority of the sorbents appearing in the recent literature.[9,12,14,35–41] Only few materials showed higher sorption capacity.[42–45]

TABLE IV. A comparison of boron sorption capacity for selected sorbents reported in the literature

Sorbent material	Uptake, mg g^{-1}	Ref.
Raw vermiculite	0.2	39
Modified vermiculite (ultrasound, 20 kHz, H_2O_2)	1.6	39
Chitosan	3.9	46
Dowex (XUS 43594.00) resin	8.5	36
Diaion CRB 02 resin	8.5	36
Rice residues	9.26	46
Glucamine-based chelate adsorbent including Diaion CRB 03	10.7	14
Glucamine-based chelate adsorbent including Chelest Fiber GRY-HW	12.4	14
Glucamine-based chelate adsorbent including Diaion CRB 05	12.7	14
Dowex 2x8 anion exchange resin	17	9
AlMg layered double hydroxide alcined at 550 °C	25.5	35
Pomegranate seed powder modified with PVA	30	46
Crosslinked chitosan	33.9	40
Chitosan with N-methylglucamine	35.1	41
Multi-hydroxyl functional hairy polymers	35.7	12
Linear chitosan	38	40
$NO_{3.}$Mg–Al layered double hydroxide	38.9	37
Cl.Mg–Al layered double hydroxide	41	37
2,3-Dihydroxybenzaldehyde modified Silica Gel	41.2	38
NanoFe-impregnated granular activated carbon	50	43
Polyethylenimine – epichlorohydrin resin	55	This work
Composite containing chitosan (as the encapsulating material) and nickel (II) hydroxide	61.4	42
Fe(3) oxide/hydroxide nanoparticles sol (NanoFe)	65	43
Magnetic porous chitosan-based microbeads	66.85	44

TABLE IV. Continued

Sorbent material	Uptake, mg g^{-1}	Ref.
Mg–Al oxide	79.9	[45]
Hydroxyl-enhanced magnetic chitosan microbeads	128.5	[44]
Sepiolite modified with HCl	178.57	[46]

CONCLUSIONS

The synthesized polyethylenimine–epichlorohydrin resin appears to be superior to a number of other sorbents for anionic boron species (borates) removal. The sorption efficiency of the resin is strongly affected by the pH that influences both the boron speciation in the solution and the surface functional groups protonation/deprotonation of the resin. In acidic environments, the surface becomes positively charged and does not favour the neutral boric acid removal. The ability of resin to adsorb boron from basic media is mainly attributed to the highly ionized quaternary amine moiety, permitting the existence of the positively charged sites (R_4N^+), necessary for interaction with borate anions. The resin best performed at pH 9.0, having a boron uptake of 55 mg L^{-1}.

The modelling of the equilibrium data indicated a homogenous boron sorption in acidic and heterogeneous sorption in alkaline environment. The homogenous sorption at pH_e 3.0 was further confirmed by the sorption kinetics. The best correlation with the experimental data was obtained for the adsorption kinetic model restricted to the case for which the adsorption equilibrium relationship is of the Langmuir type. Nevertheless, the obtained results gave ground to the assumption that the distinction between the kinetics models requires more fundamental studies of the adsorption process than afforded by the comparison of the model fit.

The sorbent under investigation shows potential to be applied for boron removal from alkaline waters and wastewaters.

SUPPLEMENTARY MATERIAL

Additional data and considerations are available electronically at the pages of journal website: http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

ИЗВОД

УКЛАЊАЊЕ БОРА ИЗ ВОДЕНИХ РАСТВОРА СМОЛОМ ПОЛИЕТИЛЕНИМИН–ЕПИХЛОРОХИДРИН

SOFIA SARRI[1], PANAGIOTIS MISAELIDES[1], DIMITRIOS ZAMBOULIS[1] и JOLANTA WARCHOŁ[2]

[1]*Department of Chemistry, Aristotle University of Thessaloniki, GR-54124 Thessaloniki, Greece* и
[2]*Department of Water Purification and Protection, Rzeszow University of Technology, Rzeszow, Poland*

Испитивано је коришћење смоле полиетиленимин–епихлорохидрин за уклањање бора из водених раствора (концентрација бора: 100–5000 mg L^{-1}) неподешених и предподешених pH (pH_{nat}, pH_{init} 8,0, 9,0 и 10,0) водених раствора коришћењем шаржне технике. Концетрације бора у растворима после сорпције одређиване су фотометријски. Резултати су указали да је уклањање бора зависно од pH повезано са протонацијом/депротонацијом површински функционалних група смоле и од специјације бора у растворима различитих pH вредности. Максимални капацитет сорпције бора уочен у растворима на pH 9,0 био је 55 mg g^{-1}, што премашује већину других комерцијалних или алтернативних сорбената. За моделовање адсорпционе равнотеже бора употребљено је пет емпиријских адсорпционих једначина (Freundlich, Langmuir, Redlich–Peterson, Langmuir–Freundlich и Toth). Моделовање резултата је идентификовало хомогену сорпцију бора из киселих и хетерогену сорпцију из алкалних раствора. При алкалним pH, неидеалност система може да потиче од различитих механизама везивања или од компетитивне сорпције различитих хемијских врста са бором. Хомогени тип сорпције бора из киселих раствора даље је потврђен проучавањем кинетике.

(Примљено 4. јула, ревидирано 25. септембра, прихваћено 30. октобра 2017)

REFERENCES

1. U.S. Agency for Toxic Substances and Disease Registry, *Toxicological Profile for Boron*, Atlanta, GE, 2010, http://www.atsdr.cdc.gov/ToxProfiles/tp26.pdf (accessed 19 June 2017)
2. U.S. Environmental Protection Agency, *Toxicological review of boron and compounds*, Report EPA 635/04/052, Washington DC, 2004, http://cfpub.epa.gov/ncea/iris/iris_documents/documents/toxreviews/0410tr.pdf (accessed 19 June 2017)
3. Scientific Committee on Health and Environmental Risks, European Commission *Derogation on the Drinking Water Directive 98/83/EC*, 2010, http://ec.europa.eu/health/scientific_committees/environmental_risks/docs/scher_o_120.pdf (accessed 19 June 2017)
4. World Health Organization, *Guidelines for Drinking-water Quality*, 4th ed., Geneva, 2011, http://apps.who.int/iris/bitstream/10665/44584/1/9789241548151_eng.pdf (accessed 19 June 2017)
5. Bundesinstitut für Risikobewertung, Stellungnahme Nr. 024/2006 des Bundesinstituts für Risikobewerung (BfR), 2006, http://www.bfr.bund.de/cm/343/hoechstmengen_fuer_ _bor_und_fluorid_in_natuerlichen_mineralwaessern_sollten_sich_an_trinkwasserregelungen_orientieren.pdf (accessed 19 June 2017)
6. T. E. Köse, N. Öztürk, *J. Hazard. Mater.* **152** (2008) 744
7. P. Koseoglu, K. Yoshizuka, S. Nishihama, U. Yuksel, N. Kabay, *Solv. Extr. Ion Exch.* **29** (2011) 440
8. K. Ooi, H. Kanoh, A. Sonoda, T. Hirotsu, *J. Ion Exch.* **7** (1996) 166
9. N. Öztürk, T. E. Köse, *Desalination* **227** (2008) 233
10. C. Y. Yan, W. T. Yi, *Environ. Prog. Sustain. Energy* **29** (2010) 450
11. P. Dydo, M. Turek, *Desalination* **310** (2013) 2
12. M. Gazi, G. Galli, N. Bicak, *Sep. Purif. Technol.* **62** (2008) 484
13. Ö. Kaftan, M. Açikel, A. E. Eroğlu, T. Shahwan, L. Artok, C. Ni, *Anal. Chim. Acta* **547** (2005) 31
14. S. Nishihama, Y. Sumiyoshi, T. Ookubo, K. Yoshizuka, *Desalination* **310** (2013) 81
15. I. Tsuboi, E. Kunugita, I. Komasawa, *J. Chem. Eng. Jpn.* **23** (1990) 480
16. C. Yan, W. Yi, P. Ma, X. Deng, F. Li, *J. Hazard. Mater.* **154** (2008) 564
17. M. Matsumoto, K. Kondo, M. Hirata, S. Kokubu, T. Hano, T. Takada, *Sep. Sci. Technol.* **32** (1997) 983
18. Y. Magara, T. Aizawa, S. Kunikane, M. Itoh, M. Kohki, M. Kawasaki, H. Takeuti, *Water Sci. Technol.* **34** (1996) 141
19. L. Melnyk, V. Goncharuk, I. Butnyk, E. Tsapiuk, *Desalination* **185** (2005) 147
20. J. Wolska, M. Bryjak, *Desalination* **310** (2013) 18

21. N. Hilal, G. J. Kim, C. Somerfield, *Desalination* **273** (2011) 23
22. N. Kabay, E. Güler, M. Bryjak, *Desalination* **261** (2010) 212
23. N. Geffen, R. Semiat, M. S. Eisen, Y. Balazs, I. Katz, C. G. Dosoretz, *J. Membr. Sci.* **286** (2006) 45
24. A. Ince, B. Karagoz, N. Bicak, *Desalination* **310** (2013) 60
25. A. D. Ebner, J. A. Ritter, H. J. Ploehn, R. L. Kochen, J. D. Navratil, *Sep. Sci. Technol.* **34** (1999) 1277
26. A. D. Eaton, L. S. Clesceri, A. E. Greenberg, *Standard Methods for the Examination of Water and Wastewater*, 19th ed., APHA, Washington DC, 2005, 1995, pp. 4–10
27. E. Baumgarten, A. Fiebes, A. Stumpe, F. Ronkel, J. W. Schultze, *J. Mol. Catal., A: Chem.* **113** (1996) 469
28. S. Kundu, W. Xia, W. Busser, M. Becker, D. A. Schmidt, M. Havenith, M. Muhler, *Phys. Chem. Chem. Phys.* **12** (2010) 4351
29. J. R. Pels, F. Kapteijn, J. A. Moulijn, Q. Zhu, K. M. Thomas, *Carbon* **33** (1995) 1641
30. S. Sarri, P. Misaelides, D. Zamboulis, L. Papadopoulou, J. Warchoł, *J. Radioanal. Nucl. Chem.* **295** (2013) 1731
31. J. Warchoł, M. Matłok, P. Misaelides, F. Noli, D. Zamboulis, A. Godelitsas, *Micropor. Mesopor. Mater.* **153** (2012) 63
32. O. Levenspiel, *Chemical reaction engineering*, J. Wiley & Sons, 3rd Ed., New York, 1999
33. K. H. Chu, *J. Hazard. Mater.* **90** (2002) 77
34. Y. S. Ho, G. Mckay, *Can. J. Chem. Eng.* **76** (1998) 822
35. E. D. Isaacs-Paez, R. Leyva-Ramos, A. Jacobo-Azuara, J. M. Martinez-Rosales, J. V. Flores-Cano, *Chem. Eng. J.* **245** (2014) 248
36. N. Kabay, I. Yilmaz, M. Bryjak, M. Yüksel, *Desalination* **198** (2006) 158
37. T. Kameda, J. Oba, T. Yoshioka, *J. Hazard. Mater.* **293** (2015) 54
38. D. Kara, *Water Air Soil Poll.* **226** (2015) 223
39. M. Kehal, L. Reinert, L. Duclaux, *Appl. Clay Sci.* **48** (2010) 561
40. D. V. Nesterov, L. S. Molochnikov, A. V. Pestov, *Russ. Chem., B+* **63** (2014) 1511
41. Y.-T. Wie, Y.-M. Zheng, J. P. Chen, *Water Res.* **45** (2011) 2297
42. H. Demey, T. Vincent, M. Ruiz, A. M. Sastre, E. Guibal, *Chem. Eng. J.* **244** (2014) 576
43. G. Zelmanov, R. Semiat, *Desalination* **333** (2014) 107
44. A. A. Oladipo, M. Gazi, *React. Funct. Polym.* **109** (2016) 23
45. T. Kameda, J. Oba, T. Yoshioka, *J. Environ. Manage.* **165** (2016) 280
46. Z. Guan, J. Lv, P. Bai, X. Guo, *Desalination* **383** (2016) 29.