BOR DERGİSİ
JOURNAL OF BORON
Journal homepage: www.journal.boren.gov.tr

Resin type and resin diameter effect on the adsorption of boron isotopes

Gonca Sağlam[1*], Zeynep Aktosun[1], Gülşah Özçelik[1], Ahmet R. Özdural[2]

[1]National Boron Research Institute, 06520 Ankara Turkey

[2] Hacettepe University, Department of Chemical Engineering, 06800 Ankara, Turkey

ARTICLE INFO

Artlice history:
Received 29 January 2016
Received in revised form 14 March 2016
Accepted 14 March 2016
Available online 24 March 2016

Keywords:
Chromatography,
stationary phase,
boron isotopes,
Langmuir adsorption
isotherm parameters

ABSTRACT

Chromatography is a technique for molecular partition in which a fluid (mobile phase) carries the material containing the mixture to be separated (sample) past or through a solid or gel (stationary phase) contained in a vessel. The stationary phase has characteristics that delay the passage of some molecular components of the sample more than the passage of others causing them to separate in the mobile phase emerging from the column. The selection of stationary phase is one of the key factors for reaching an optimum separation in chromatographic applications. The scope of this work is to investigate the effect of resin type and diameter from the point of Langmuir adsorption isotherm parameters of ^{10}B and ^{11}B isotopes for chelating resin and weak base anion exchange resin.

1. Introduction

Chromatography is a widely used and highly selective process of separation, employed in the separation of complex mixtures of which the overall product yield of sugars, proteins, pharmaceuticals, fine chemicals, flavorings, foods, enantiomers and isomers….etc. is governed by the individual yields of discrete operations. It is admitted by several researchers that no other separation method is as powerful and generally applicable as is chromatography [1-4].

The successful design and the operation of chromatographic separations require the optimization of a large number of parameters which affect the separation in interacting fashion. Resin which is used as stationary phase in chromatographic separations plays a key role in order to increase resolution as well as productivity of the chromatographic system.Adsorption isotherm-expressions give the relationship between the stationary phase and liquid phase concentrations of components. In other words, adsorption isotherms relates the stationary phase concentration that is in equilibrium with the liquid phase concentration. Thus the easiest and accurate way to select stationary phase is to determine the suitable adsorption isotherm expression as well as the adsorption isotherm constants that belongs to that expression. Several types of adsorption isotherm models have been introduced to describe the adsorption behavior of chromatography columns such ascompetitive Langmuir isotherm, bi-Langmuir isotherm, Freundlich isotherm and linear adsorption isotherm [5-11]. Among these isotherms, competitive Langmuir adsorption isotherm is the commonly used one that express the equilibrium stationary phase and liquid phase concentrations for most enantiomer, protein and concentrated sugar mixtures [11-14].

The competitive Langmuir isotherm model assumes monolayer coverage of the adsorbate molecules over a homogeneous adsorbent surface [15-16] and the rate of adsorption and desorption are equal for each component in the case of equilibrium. The Competitive Langmuir adsorption isotherm equationsfor ^{10}B and^{11}B isotopes are given in Eq. (1).

$$q_{10B} = \frac{qm_{10B}\ c_{10B}}{1 + K_{10B}\ c_{10B} + K_{11B}\ c_{11B}} \quad (1a)$$

$$q_{11B} = \frac{qm_{11B}\ c_{11B}}{1 + K_{10B}\ c_{10B} + K_{11B}\ c_{11B}} \quad (1b)$$

*corresponding author: gonca@boren.gov.tr

In Eq. (1) qm_{10B} (mg_{10B}/cm^3_{resin}) and qm_{11B}(mg_{11B}/cm^3_{resin}) are the maximum ^{10}B and ^{11}B isotope adsorption capacities of the resin respectively, whereas K_{10B} (mg_{10B} /cm^3) and K_{11B} (mg_{11B} /cm^3) are the adsorption isotherm constants, that states the affinity of ^{10}B and ^{11}B isotopes to the resin phase.

There are several types of resins for boron isotope enrichment with ion exchange principle such as weak base anion exchange resin, strong base anion exchange resin and chelating resins. Weak or strong base anion exchange mechanism is depends on anion exchange between the anions in the liquid phase and the functional groups in the resin phase whereas chelating mechanism is much more complicated such that functional groups in the resin phase is specialized only specific anion in the liquid phase. Thus resin selection is one of the most important parameter for optimum separation of components. Not only the resin type but also resin particle diameter affects the resolution of components to be separated. It is well known that as the resin particle diameter decreases, the surface area of resin increases so that H.E.T.P. of chromatographic column increases. Briefly, decrease in particle diameter, increases the resolution of chromatographic application [16-19] but while decreasing particle diameter, the pressure drop along the column should be considered.

In this study, chelating and weak base ion exchange resin types are compared for the adsorption of ^{10}B and ^{11}B isotopes. In addition to that the effect of resin particle diameter is investigated in terms of competitive Langmuir adsorption isotherm parameters of boron isotopes.

2. Materials and methods

In the experimental part of this study, batch uptake experiment are performed for 100, 500, 1000, 2000, 3000, 4000, 5000, 6000, 7000 and 8000 mg/L boric acid (Eti Mine Works General Directorate) initial concentrations. Equilibrium time is 3 hours and 400 rpm rotational speed is applied for ten different, 50 mL boric acid solution at room temperature.

Relite CRB03 (Mitsubishi Chemical, Japan) chelating resin and Diaion WA21 (Mitsubishi Chemical, Japan) weak base anion exchange resin is investigated for boron isotope adsorption mechanism. In addition to that particle diameter effect of chelating resin, Relite CRB03 is studied. The average particle diameter of Relite CRB03 resin is 580 μm and 270 μm and average particle diameter of Diaion WA21 is 580 μm. The particle size distribution of resins are given is Fig. (1).

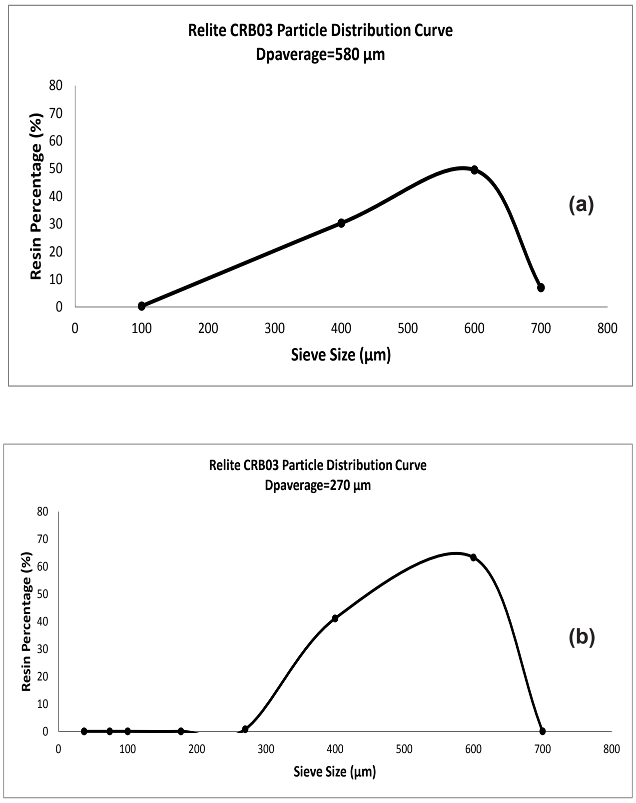


Figure 1. The particle size distribution curves of chelating resin, Relite CRB03, (a) $Dp_{average}$=580 μm, (b) $Dp_{average}$=270 μm

In batch uptake experiments, 1 g resin that is regenerated with 0.025 M HCl (Merck, U.S.A.) solution and distillate water, is used for each boric acid solution. Initial and equilibrium boron isotope concentrations are analyzed with ICP-MS (Perkin Elmer ELAN 9000, U.S.A.). The analysis results of bulk liquid boron isotope concentration show that after 4 hours the equilibrium is reached between the stationary and liquid phase as the boron isotope concentrations in liquid phase remain constant after 20 hours.

3. Results and discussions

The equilibrium resin phase concentration is calculated from the difference between the initial and equilibrium concentrations of ^{10}B and ^{11}B isotopes, given in Eq. (2a) and (2b) respectively.

$$q_{eq10B} = \frac{\left(C_{eq10B} - C_{010B}\right).V_{solution}}{m_{resin} / \rho_{resin}} \qquad (2a)$$

$$q_{eq11B} = \frac{\left(C_{eq11B} - C_{011B}\right).V_{solution}}{m_{resin} / \rho_{resin}} \qquad (2b)$$

In equation q_{eq10B} (mg_{10B}/cm^3_{resin}) and q_{eq11B} (mg_{11B}/cm^3_{resin}) are the equilibrium stationary phase concentrations of ^{10}B and ^{11}B isotopes respectively, C_{010B} (mg_{10B}/cm^3_{liquid}) and C_{011B} (mg_{11B}/cm^3_{liquid}) are the initial concentrations of ^{10}B and ^{11}B isotopes respectively, C_{eq10B} (mg_{10B}/cm^3_{liquid}) and C_{eq11B} (mg_{11B}/cm^3_{liquid}) are the equilibrium concentrations of ^{10}B and ^{11}B isotopes in the liquid phase respectively, $V_{solution}$(mL) is the solution volume, m_{resin} (mg) is the weight of resin and ρ_{resin} (mg/mL) is the density of the resin.

The competitive Langmuir adsorption isotherm of chelating resins 580 µm average particle diameter Relite CRB03, 270 µm average particle diameter Relite CRB03 and weak base anion exchange resin 580 µm average particle diameter Diaion WA21 for ^{10}B and ^{11}B isotopes are given in Fig.(2), (3) and (4).

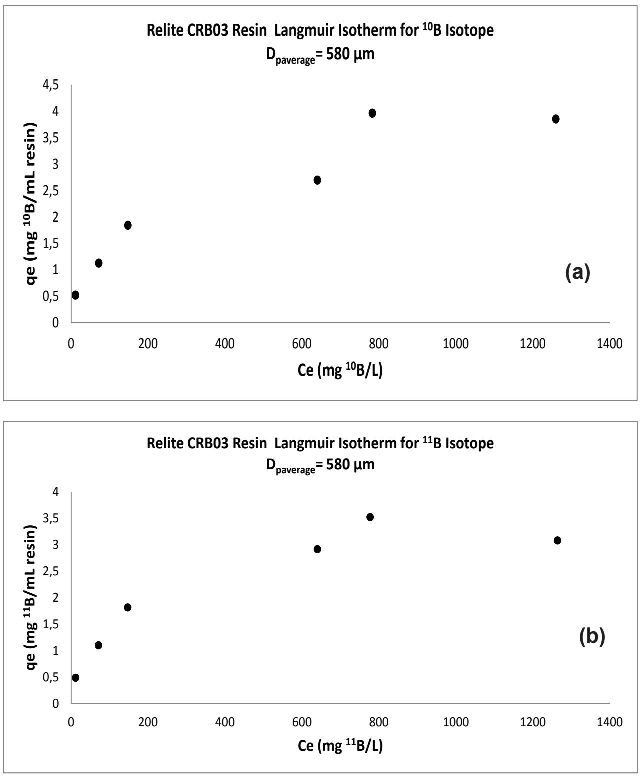
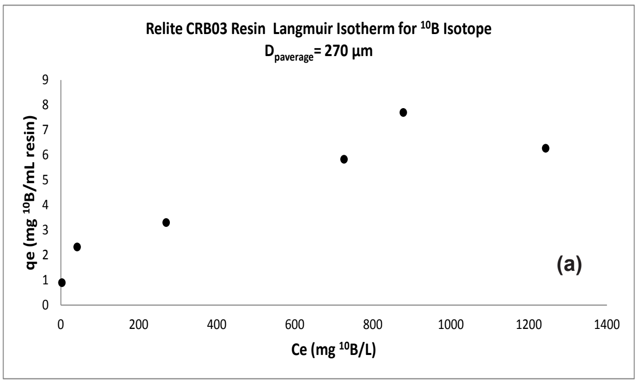


Figure 2. Competitive Langmuir adsorption isotherm of Relite CRB03 chelating resin of 580 µm average particle diameter for (a) ^{10}B isotope and (b) ^{11}B isotope.



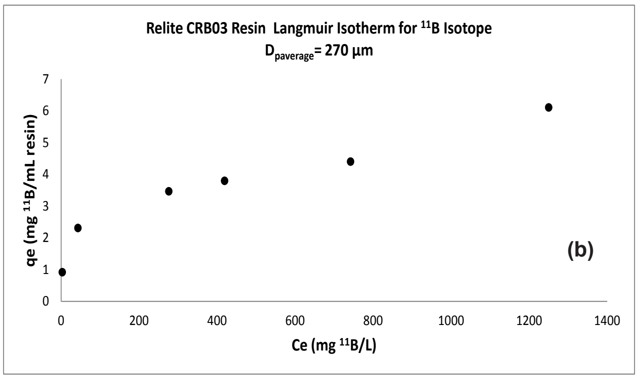


Figure 3. Competitive Langmuir adsorption isotherm of Relite CRB03 chelating resin of 270 µm average particle diameter for (a) ^{10}B isotope and (b) ^{11}B isotope.

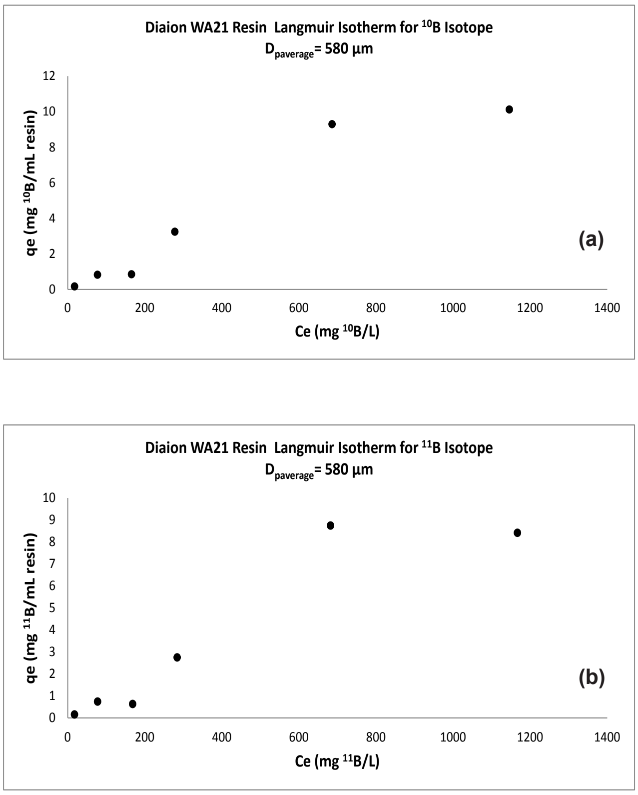


Figure 4. Competitive Langmuir adsorption isotherm of Diaion WA21 weak base anion exchange resin of 580 µm average particle diameter for (a) ^{10}B isotope and (b) ^{11}B isotope.

The competitive Langmuir adsorption isotherm constants are calculated from the linearization of competitive Langmuir adsorption isotherm expression. The y-intercept of the linearized ^{10}B isotherm curve corresponds to $K_{10B}/qm_{10B}$and the slope of the linearized curveequal to $1/qm_{10B}$ value of ^{10}B isotope whereas the y-intercept of the linearized ^{11}B isotherm curve corresponds to K_{11B}/qm_{11B} and the slope of the linearized curve equal to $1/qm_{11B}$ value of ^{11}B isotope for the selected resin. In Tables 1 and 2 the adsorption isotherm parameters are given for chelating and weak base anion exchange resins.

Table 1. Competitive Langmuir Adsorption Isotherm Parameters of ^{10}B Isotope

	RELITE CRB03 Resin	RELITE CRB03 Resin	DIAION WA21 Resin
Average Resin Diameter (µm)	580	270	580
qm_{10B}(mg/mL)	2.73	4.51	16.31
K_{10B}(mg/mL)	4.87x10^{-2}	1.09x10^{-2}	1.70
R^2 of Linearized Isotherm Curve	0.944	0.937	0.988

Table 2. Competitive Langmuir Adsorption Isotherm Parameters of ^{11}B Isotope

	RELITE CRB03 Resin	RELITE CRB03 Resin	DIAION WA21 Resin
Average Resin Diameter (µm)	580	270	580
qm_{11B}(mg/mL)	2.65	3.86	6.11
K_{11B}(mg/mL)	5.00x10^{-2}	9.23x10^{-3}	6.67 x10^{-1}
R^2 of Linearized Isotherm Curve	0.961	0.957	0.974

From Table 1 and 2 it is clearly realized that three of all of the resins are higher affinity to ^{10}B isotope as the three of the resins have higher ^{10}B maximum adsorption capacity values (qm) than the that of ^{11}B whereas the constant isotherm parameter, K that is inversely proportional with particle affinity is higher for ^{10}B isotope at Relite CRB03 with small particle diameter and Diaion WA21. On the other hand, this value is higher for ^{11}B isotope at large particle diameter Relite CRB03. In addition to that as the particle diameter decreases, the adsorption capacity of the resin increases because of increasing resin surface area.

Researchers suggest that the difference between the tetrahedral coordinational geometry of boron complex of ^{10}B isotope in the resin and the planar trigonal coordinational geometry of boron complex in solution phase result in fractionation of boron isotopes. With N-methyl glucamine type resins, it is observed that when pH < 7, adsorption of ^{10}B isotope to the resin phase is greater than that of ^{11}B and for the case of pH values greater than 11, no enrichment in boron isotopes occur [20, 21]. After regeneration with dilute HCL solution, the pH of N-methyl glucamine type resin, Relite CRB03 is 3.03 whereas the pH of weak base anion exhange resin, Diaion WA21 is 5.25. When chelating and weak base anion exchange resins are compared from the viewpoint of boron adsorption capacity Diaion WA21 is superior than Relite CRB03 since the maximum adsorption capacity, qm of Diaion WA21 is the highest among that of other resins, for both ^{10}B and ^{11}B isotopes. On the other hand, as the medium pH of Relite CRB03 is more acidic the enrichment of boron isotopes in other words resolution parameter for this resin is greater than the that of Diaion WA21. Thereby, ^{10}B isotope enrichment in stationary phase meanwhile ^{11}B isotope enrichment in liquid phase is greater for Relite CRB03. Sonoda et. al [22, 23] revealed the effectiveness of N-methyl glucamine type resins in the scope of boron isotope enrichment with column chromatography whereas weak base anion exchange resins are preferred by several researchers for boron isotope enrichment [21, 24].

4. Concluding remarks

In this study the effect of resin type and resin particle diameter is investigated for ^{10}B and ^{11}B isotopes in terms of competitive Langmuir adsorption isotherm constants. It is concluded that the best resin from the point of isotope productivity is weak base anion exchange resin as it has the highest maximum adsorption capacity. But with regard to boron isotope selectivity it is logical to choose chelating resin, Relite CRB03 with small particle diameter since it has the lowest constant isotherm parameter, K and pH value in the adsorption medium.

References

[1] Sewell P., Clarke B., Chromatographic separations, New York, Wiley, 1988.

[2] Jonsson J. A., Chromatographic theory and basic principles, New York, Marcel Dekker, 1987.

[3] Braithwaite A., Smith FJ., Chromatographic methods. 5th ed. London Blackie, 1996.

[4] Skoog D. A., West D. M., Holler F. J., Crouch S. R., Fundamentals of analytical chemistry. 8th ed. Thomson-Brooks Cole, Belmont, 2003.

[5] Lim B. G., Ching C. B., Tan R. B. H., Determination of competitive aIsotherm of enantiomers on a dual-site adsorbent, 213-228, 1995.

[6] Ravald L., Fornstedt T., Theoretical study of the accuracy of the elution by characteristic points method for Bi-Langmuir isotherms, 13th International Symposium on Preparative and Process Chromatography-Journal of Chromatography A, 908, 111–130, 26 January 2001.

[7] Gentilini A., Migliorini C., Mazzotti M., Morbidelli M., Optimal operation of simulated moving-bed units for non-linear chromatographic separations: II. Bi-Langmuir Isotherm, Journal of Chromatography A, 805, 37–44, 1 May 1998.

[8] Umpleby R. J., Baxter S. C., Chen Y., Shah R. N, Shimizu K. D., Characterization of molecularly imprinted polymers with the Langmuir−Freundlich isotherm, August 23, 2001

[9] Guiochon G., Felinger A., Shirazi D. G. G., Fundamentals of preparative and nonlinear chromatograph, Second Edition, 67-216, 2006.

[10] Hashem N. N., Optimization of chiral separation of nadolol by simulated moving bed technology, pHD Thesis, The University of Western Ontario, December 2012.

[11] Ching C. B., Ho C., Ruthven D. M., An improved adsorption process for the production of high-fructose syrup, AICHE Journal, 32, 1876–1880, 1986.

[12] Choi Y. J., Han S. K., Chung S. T., Row K. H., Separation of racemic bupivacaine using simulated moving bed with mathematical model, Biotechnology and Bioprocess Engineering , 12, 625-633, 2007.

[13] Asnin L., Kaczmarski K., Guiochon G., The adsorption of naproxen enantiomers on the chiral stationary phase whelk-O1 under reversed-phase conditions: The effect of buffer composition,Journal of Chromatography A, 1217, 7055-7064, 2010.

[14] Sağlam G., Manufacture of simulated moving bed and annular chromatography systems: Assessment of BSA purification performance in annular chromatography, Master Thesis, Hacettepe University, Chemical Engineering Department, 2009.

[15] Lorenz K., Maga J., Use of gas-liquid chromatography for quality evaluation of dry egg products, Journal of Food Science, 36 (6) 936–939, September 1971.

[16] Kim J. I. I., Hong S. B., Row K. H., Effect of particle size in preparative reversed-phase high-performance liquid chromatography on the isolation of epigallocatechin gallate from Korean Green Tea, Journal of Chromatography A, 275–280, 2002.

[17] Liu H., Finch J. W., Lavallee M. J., Collamati R. A., Benevides C. C., Gebler J. C., Effects of column length, particle size, gradient length and flow rate on peak capacity of nano-scale liquid chromatography for peptide separations, Journal of Chromatography A, 1147, 30–36, 2007.

[18] Poe D. P., Schroden J. J., Effects of pressure drop, particle size and thermal conditions on retention and efficiency in supercritical fluid chromatography, Journal of Chromatography A, 1216, 7915–7926 , 2009.

[19] Unger K. K., Lamotte S., Machtejevas E., Column technology in liquid chromatography, liquid chromatography: Fundamentals and instrumentation, Chapter 3, 41-86, Elsevier, 2013.

[20] Sonoda, A., Makita, Y., Ooi, K., Takagi, N., Hirotsu, T., pH-dependence of the fractionation of boron isotopes with N-methyl-D-glucamine resin in aqueous solution systems, Bulletin of the Chemical Society of Japan, 73, 1131-1133, 2000.

[21] Kakihana, H., Kotaka, M., Satoh, S., Nomura, M., Okamoto, M., Fundamental studies on the ion-exchange separation of boron isotopes, Bulletin of the Chemical Society of Japan, 50, 158-163, 1977.

[22] Sonoda, A., Makita, Y., Hirotsu T., Boron isotope fractionation in column chromatography with glucamine type resins, Journal of Nuclear Science and Technology, 43,437-440, 2006.

[23] Sonoda, A., Makita, Y., Hirotsu T., Boron isotope fractionation in column chromatography with glucamine type fibers, Journal of Nuclear Science and Technology, 6, 117-121, 2008.

[24] Sakuma Y., Aida M., Okamoto M., Kakihana H., Boron isotope separation by ion exchange chromatography using weakly basic anion exchange resin, Bulletin of the Chemical Society of Japan, 53, 1860-1863, 1980.