

Removal of Boron from Waste Waters by Ion-Exchange in a Batch System

Pelin Demirçivi, and Gülhayat Nasün-Saygılı

Abstract—Boron minerals are very useful for various industrial activities, such as glass industry and detergent industry, due to its mechanical and chemical properties. During the production of boron compounds, many of these are introduced into the environment in the form of waste. Boron is also an important micro nutrient for the plants to vegetate but if it exists in high concentrations, it could have toxic effects. The maximum boron level in drinking water for human health is given as 0.3 mg/L in World Health Organization (WHO) standards. The toxic effects of boron should be noted especially for dry regions, thus, in recent years, increasing attention has been paid to remove the boron from waste waters. In this study, boron removal is implemented by ion exchange process using Amberlite IRA-743 resin. Amberlite IRA-743 resin is a boron specific resin and it belongs to the polymerizate sorbent group within the aminopolyol functional group. Batch studies were performed to investigate the effects of various experimental parameters, such as adsorbent dose, initial concentration and pH, on the removal of boron. It is found that, when the adsorbent dose increases removal of boron from the liquid phase increases. However, an increase in the initial concentration decreases the removal of boron. The effective pH values for removal of boron are determined between 8.5 and 9. Equilibrium isotherms were also analyzed by Langmuir and Freundlich isotherm models. The Langmuir isotherm is obeyed better than the Freundlich isotherm.

Keywords—Amberlite resin, boron removal, ion exchange, isotherm models.

I. INTRODUCTION

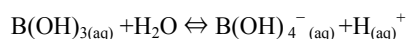
DEVELOPMENT of the ecologically and economically appropriate technology to remove the toxic compounds of boron from different waters is a pressing goal over the entire world. This is due to a wide spreading of this element in both natural waters and waste waters [1]-[6]. Boron has a number of minerals, in nature mostly calcium and/or sodium borates, such as colemanite ($2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), ulexite ($\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 5\text{B}_2\text{O}_3 \cdot 16\text{H}_2\text{O}$), tinkal ($\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$), etc. [7], [8].

There is a variety of application including various boron fertilizers, insecticides, corrosion inhibitors in anti-freeze formulations for motor vehicle and other cooling system, buffers in pharmaceutical and dyestuff production, and the use of boron compounds for moderator in nuclear reactor, where

anthropogenic water-soluble boron compounds are discharged to aqueous environment. Boron is normally in very low amounts in soil and irrigation waters, but it accumulates very fast in soils irrigated with boron-containing wastewaters because of difficulty of washing it. Boron compounds passing to soil, surface waters and ground waters form many complexes with heavy metals, such as Pb, Cd, Cu, Ni, etc. and these complexes are more toxic than heavy metals forming them. Although little amount of boron is a nutrient for some plants, its excessive amount affects badly the growth of many agricultural products. The World Health Organization (WHO) has given a recommendation of below 0.3 mg/L boron for the quality of drinking water [9].

There is a small range between boron deficiency and boron toxicity in plants [10]. Boron has been shown to play a role in carbohydrate metabolism, sugar translocation, pollen germination, hormone action, normal growth and functioning of the apical meristem, nucleic acid synthesis, and membrane structure and function [11].

In aqueous environments, boron is mainly present as boric acid and partially as borate ions according to the dissociation reaction ($K_a = 6 \times 10^{-10}$, pK_a 9.1) as shown in the following equation [9]:



Among several methods of boron removal from aqueous solutions, the use of boron-selective resins seems to have still the highest importance. Some studies on application of flying ashes or natural sorbents, inorganic adsorbents show boron-selective resins based on macroporous polystyrene matrices with N-methyl glucamine ligand as the best sorbent. Simonnot et al. have reviewed the methods of boron removal from drinking water. Among them, they have pointed that the use of boron-selective resins is the most efficient one [12]-[21]. Numerous researchers studied boron removal and/or recovery from wastewaters. Amberlite IRA 743, a boron specific resin, was used in boron removal from geothermal waters containing 19 mg/L boron and it was found that 99% of boron from geothermal water could be removed [22].

This study focuses on boron removal by means of ion exchange process. Batch experiments were studied to determine the effects of several parameters such as, initial solution concentration, pH, and amount of adsorbent on boron removal from wastewater. Langmuir and Freundlich isotherm models were used for the evaluation of findings.

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II. EXPERIMENTAL

In this study, Amberlite IRA-743 resin was procured from Merck Darmstadt–Germany. Boric acid which contains 56.3% B_2O_3 was supplied from Eti Maden. The other chemicals used were of analytical reagent grade supplied by Merck Darmstadt–Germany.

Boron stock solution (1000 mg/L) was prepared by weighing in analytical balance and dissolving an appropriate quantity of boric acid (H_3BO_3) in distilled water, and the working solutions were prepared by diluting this solution. In this work, 20 mg/L, 40 mg/L and 60 mg/L boron solutions were prepared and used in batch experiments. To observe the effect of adsorbent dosage on boron removal, different amounts of Amberlite resin were used (0.1-10 g). In order to investigate the effect of pH, initial pH of solution was varied from 2 to 10.

The experiments were carried out using the batch method. Batch ion exchange experiments were conducted using various amounts of resin with 50 ml of solutions containing boron ions of desired concentrations at constant temperatures in 250 ml flasks. pH was adjusted to the desired level with NaOH and HCl solutions. The samples were agitated at constant speed with magnetic stirrer during 24 h and then filtered to get the clear solution. The clear solution was analyzed in order to determine its boron content by using volumetric method. The pH values at equilibrium after 24 h were measured. All experiments have been taken at the room temperature.

III. RESULTS AND DISCUSSION

A. Effect of Adsorbent Quantity and Initial Boron Concentration

The effect of adsorbent quantity was examined by using various amounts of Amberlite IRA-743 resin. In experiments, initial boron concentration was kept constant. Then experiments were repeated for various boron concentrations while the resin amount was kept constant. The results are shown graphically in Fig. 1 and Fig. 2. Initial and final boron concentrations were measured by using volumetric method. In order to obtain the sorption capacity (q), the amount of ions adsorbed per unit mass of adsorbent (mg/g) was given in (1):

$$q = [(c_0 - c)/m] \times V \quad (1)$$

where c_0 and c are the initial and final boron concentration (mg/L) in the solution, m the amount of the adsorbent used (g) and V the volume of the aqueous phase (L). The yield or amount of boron retained is given in (2):

$$\text{Removal efficiency} = [(c_0 - c)/c_0] \times 100 \quad (2)$$

Fig. 1 shows that the removal efficiency increased with increasing amount of adsorbent. It can also be seen that the efficiency decreased with increasing boron concentration. Maximum efficiency (98.86%) was obtained by using 7.01 g adsorbent and 20 mg/L initial boron concentration.

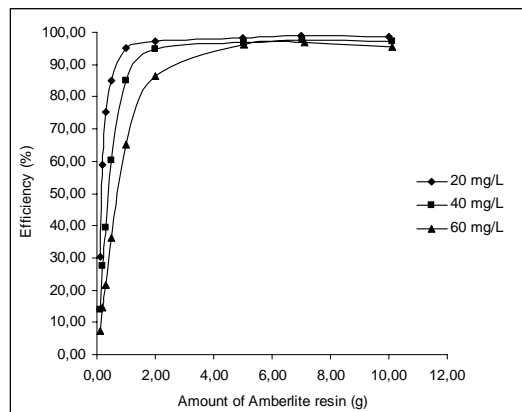


Fig. 1 Effects of adsorbent amount and initial concentration on boron removal efficiency

Isotherms of the adsorption system were shown in Fig. 2 which demonstrated boron removal increased with increasing the amount of adsorbent. Increasing resin/solution ratio that means increasing the resin-solution contact surface causes higher boron removal efficiency.

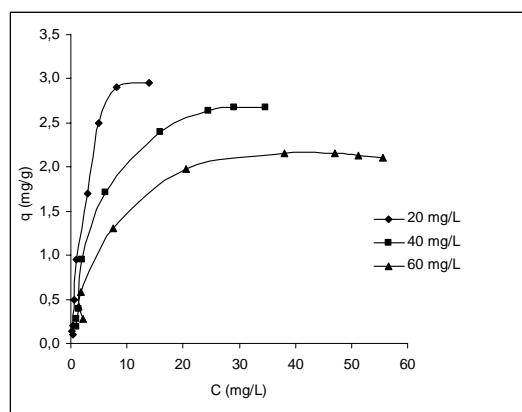


Fig. 2 Adsorption isotherm (c_0 : 20-60 mg/L; m : 0.1-10 g)

B. Isotherm Model

The relationship between the amount of boron adsorbed and the boron concentration remaining in solution is described by an isotherm. The analysis of the isotherm data is important to develop an equation which accurately represent the results and which could be used for design purposes. In order to investigate the sorption isotherm Langmuir and Freundlich isotherm models were analyzed to quantify adsorption capacity of Amberlite resin. Langmuir isotherm model is based on assuming a monolayer sorption onto a surface with a fixed number of well defined sites. The isotherm is given in (3):

$$q = (K_L c)/(1 + a_L c) \quad (3)$$

Rearranging the Langmuir equation gives (4), which is linear.

$$c/q = (1/K_L) + (a_L/K_L) \times c \quad (4)$$

q : equilibrium concentration of adsorbate in solid phase (mg/g)

c : equilibrium concentration of adsorbate in liquid phase (mg/L)

K_L/a_L : sorption capacity (mg/g)

The coefficients K_L and a_L can thus be determined by plotting c/q versus c . Langmuir isotherm model correlation coefficients are given in Table I:

TABLE I
LANGMUIR ISOTHERM DATA

c (mgL ⁻¹)	K_L (1/g)	a_L (1/mg)	R^2
20	0,85	0,19	0,91
40	0,42	0,12	0,97
60	0,28	0,11	0,97

Freundlich isotherm model gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. The isotherm is derived to model the multilayer adsorption and relates the uptake of solute onto the exchanger to the solution concentration, as shown in (5):

$$q = K_F \times c^{\frac{1}{n}} \quad (5)$$

The equation may be linearized by taking the logarithm of both sides of (5) and can be presented as shown in (6):

$$\log q = \log K_F + (1/n) \log c \quad (6)$$

q : equilibrium concentration of adsorbate in solid phase (mg/g)

c : equilibrium concentration of adsorbate in liquid phase (mg/L)

K_F, n : Freundlich constants related to the adsorption capacity and intensity

The numerical value of $1/n < 1$ indicates that adsorption capacity is only slightly suppressed at lower equilibrium concentrations. The values of K_F and n can be calculated from the intercepts and slopes of the plots of each isotherm. The correlation coefficients data of Freundlich isotherm model are given in Table II:

TABLE II
FREUNDLICH ISOTHERM DATA

c (mg/L)	K_F	n	R^2
20	0,53	1,2	0,91
40	0,32	1,49	0,89
60	0,34	2,01	0,88

According to the correlation coefficients of both isotherm models, Langmuir isotherm best represents the equilibrium adsorption of boron on the Amberlite resin.

C. Effect of pH

The removal processes and reactivity of boron in solutions are influenced by pH in a significant way. In this section, the effect of pH on boron removal was analyzed and found that pH is a considerably important control parameter for boron removal processes. The experimental results obtained are shown in Fig. 3. It can be seen that boron selectivity is efficient at pH 8.5-9. The amount of boron adsorbed depends on the distribution of $B(OH)_3$ and $B(OH)_4^-$ which are controlled by pH of the solution. It is the point at which the borate ion predominance starts to increase according to the acid-base equilibrium of boric acid. These two species compete for the adsorption on the resin. The tetrahedral $B(OH)_4^-$ becomes dominant species at pH between 9 and 10 for total boron concentration less than 3000 mg/L. It is also known that, the Amberlite resin shows high selectivity for the boron at basic pH and works as a chelating resin in basic media in its free amine form. The boron complexation at basic pH is carried out by the hydroxyl groups which have different affinity for the species $B(OH)_3$ and $B(OH)_4^-$ [23]-[25].

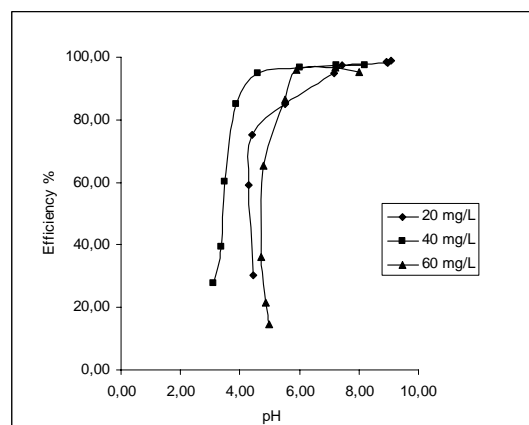


Fig. 3 Effect of pH on boron removal efficiency

IV. CONCLUSION

In the present study, the removal of boron from aqueous solution was investigated by using Amberlite IRA-743 resin. The following results are determined from the experiments;

All the batch analyses showed that Amberlite IRA-743 resin efficiency is reasonably high on boron removal. The results show that boron removal decreased with increasing boron concentration. Maximum boron removal was obtained with minimum solution concentration (20 mg/L) with 98.86% yield. The other removal yields for initial solution concentrations 40 mg/L and 60 mg/L are 97.46% and 96.89%, respectively. Amount of resin is proportional with boron removal efficiency due to increase in the resin surface area. Compared to the Freundlich isotherm, the Langmuir isotherm model represented the measured sorption data well. This indicates that the monolayer adsorption occur.

REFERENCES

- [1] Col, M. & Col, C., Environmental boron contamination in waters of Hisarcik area in the Kutahya Province of Turkey, *Food Chem. Toxicol.*, 41, pp. 1417–1420, 2003.
- [2] Klimenko, I.A., Polyakov, V.A., Sokolovskii, L.G., Aksenova, O.I., Skvortsova, O.Yu. & Okhrimenko, S.E., The sanitary status of natural waters of the territory of Moscow (according to the results of the examination of chemical and radionuclide composition), *Gig. Sanit.*, 5, pp.7–11, 2003.
- [3] Coughlin, J.R., Sources of human exposure: overview of water supplies as sources of boron, *Biol. Trace Elem. Res.*, 66, pp. 87–100, 1998.
- [4] Vengosh, A., The isotopic composition of anthropogenic boron and its potential impact on the environment, *Biol. Trace Element Res.*, 66, pp.145–151, 1998.
- [5] Barth, S., Application of boron isotopes for tracing sources of anthropogenic contamination in groundwater, *Water Res.*, 32, pp. 685–690, 1998.
- [6] Badruk, M., Kabay, N., Demircioglu, M., Mordogan, H. & Ipekoglu, U., Removal of boron from wastewater of geothermal power plant by selective ionexchange resins, *J. Sep. Sci. Technol.*, 34, pp. 2981–2995, 1999.
- [7] Barth, S., Application of boron isotopes for tracing sources of anthropogenic contamination in ground water, *Wat. Res.*, 32, pp. 685–690, 1998.
- [8] Boncukcuoglu, R., Kocakerim, M.M., Kocadagistan, E. & Yilmaz, M.T., Recovery of boron of the sieve reject in the production of borax, resources, conservation and recycling, 37(2), pp. 147–157, 2003.
- [9] Yilmaz, A.E., Boncukcuoglu, R., Yilmaz, M.T. & Kocakerim, M.M., Adsorption of boron from boron-containing wastewaters by ion Exchange in a continuous reactor, *J. Hazard. Mater.*, 117, pp. 221–226, 2005.
- [10] Parks, J.L. & Edwards, M., *Crit. Rev. Environ. Sci. Technol.*, 35, pp. 81–114, 2005.
- [11] Howe, P.D., *Biol. Trace Elem. Res.*, 66, pp. 153–166, 1998.
- [12] Polat, H., Vengosh, A., Pankratov, I. & Polat, M., *Desalination*, 164, pp. 173–188, 2004.
- [13] Inukai, Y., Tanaka, Y., Matsuda T., Nikara, N., Yamada, K., Nambu, N., Itoh, T., Ooi, K., Kaida, Y. & Yasuda, S., *Anal. Chim. Acta*, 511, pp. 261–265, 2004.
- [14] Smith, B.M., Owens, J.L., Bowman, C.H. & Todd, P., *Carbohydr. Res.*, 308, pp. 173–179, 1998.
- [15] Ay, A.N., Karan-Zumreoglu, B. & Temel, A., *Micropor. Mesopor. Mater.*, 98, pp. 1–5, 2007.
- [16] Seyhan, S., Seki, Y., Yurdakoc, M. & Merdivan, M., *J. Hazard. Mater.*, 146, pp. 180–185, 2007.
- [17] Seki, Y., Seyhan, S. & Yurdakoc, M., *J. Hazard. Mater.*, 138(1), pp. 60–66, 2006.
- [18] Karahan, S., Yurdakoc, M., Seki, Y. & Yurdakoc, K., *J. Colloid Interf. Sci.*, 293(1), pp. 36–42, 2006.
- [19] Yurdakoc, M., Seki, Y., Karahan, S. & Yurdakoc, K., *J. Colloid Interf. Sci.*, 286(2), pp. 440–446, 2005.
- [20] Simonnot, M.O., Castel, C., Nikolai, M., Rosin, C., Sardin, M. & Jaufferet, H., *Water Res.*, 34, pp. 109–116, 2000.
- [21] Kabay, N., Sarp, S., Yuksel, M., Arar, Ö. & Bryjak, M., Removal of boron from seawater by selective ion exchange resins, *Reactive & Functional Polymers*, 67, pp. 1643–1650, 2007.
- [22] Hanay, A., Boncukcuoglu, R., Kocakerim, M.M. & Yilmaz A.E., *Fresen. Environ. Bull.*, 12(10), pp. 1190, 2003.
- [23] Garcia-Soto, M.M.F. & Camacho, E.M., Boron removal by process of chemisorption, Solvent Extraction and Ion Exchange, 23, pp. 741–757, 2005.
- [24] Cengeloglu, Y., Tor, A., Arslan, G., Ersoz, M. & Gezgin, S., Removal of boron from aqueous solution by using neutralized red mud, *Journal of Hazardous Materials*, 2006.
- [25] Lou, J., Modelling of boron sorption equilibrium and kinetic studies of ion exchange with boron solution, PhD Thesis, Oklahoma State University, USA, 1997.