

## Comparative Study of Boron Removal from Reverse Osmosis Permeate Using Ion Exchange Resins

Mohammed, I Y<sup>1, 2\*</sup>, Garba, K<sup>2</sup>, Mandara, S D<sup>1</sup>, Saba A M<sup>3</sup>, Sule, U D<sup>3</sup> and Ahmed, M<sup>3</sup>

<sup>1</sup>School of Chemical and Environmental Engineering, the University of Nottingham Malaysia Campus, Jalan Broga 43500 Semenyih, Selangor, Darul Ehsan Malaysia

<sup>2</sup>Chemical Engineering Department, Abubakar Tafawa Balewa University P.M.B 0248, Bauchi

<sup>3</sup>Chemical Engineering Department, the Federal Polytechnic P.M.B 55, Bida, Nigeria

### Abstract

Reverse osmosis (RO) is the most commonly used desalination technology worldwide primarily due to its lower cost and simplicity. However, rejection of low molecular weight substances such as boron remains one of its challenges. Comparative study of boron removal from reverse osmosis permeate was carried out using Purolite S110 and Purolite S108 in batch and column studies. Overall performances of S108 were found better than that of S110. This characteristic of S108 was attributed to its improved surface area. The sorption kinetics of both resins in the batch process followed Lagergren pseudo-second order. Shrinking core model (SCM) was applied for the process kinetics and chemical reaction was found to be the rate limiting step for S110 while film diffusion controlled S108 process. In the column process, increasing flow rate led to reduction in boron removal owing to less contact time between the boron solution and the resin. Breakthrough curves were established and Yoon-Nelson model was applied for the kinetics. The column capacity was found to be 0.34eq/L and 0.40eq/L for process with S110 and S108 respectively. Finally, it can be concluded that both resins can be used to lower boron level in reverse osmosis permeate for irrigation application.

**Keywords:** Reverse osmosis; boron; desalination; Purolite<sup>R</sup>; sorption kinetics; resin

**\*Corresponding author:** Isah Yakub Mohammed ([chemicalmyhib@yahoo.com](mailto:chemicalmyhib@yahoo.com)) Phone: +601 1360 59783

## Introduction

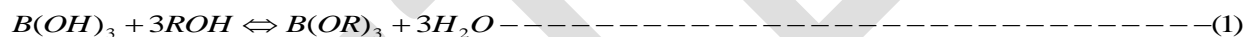
Water shortage has become a global concern. This is recognized by the growing demands on the available water resources to satisfy human, industrial and agricultural needs. Several factors are responsible for this problem which includes rapid growth in population, economic development and the resulting contamination among others. Numerous strategies have been developed towards increasing water supply such as reclamation, reuse and recycling of raw water, waste water and seawater desalination. Seawater desalination appeared to be the most favorable method of addressing the water challenge for all applications [1]. This is due to the rapid increase in number of desalination plant across the globe in recent times [2]. According to Global Water Intelligence [2], the contracted capacity of desalination plant recorded about 43% growth in 2007 relative to what was obtained in 2006 (6.8million m<sup>3</sup>/day). Similar increases were also recorded in 2008 and 2009. In 2013, the total global desalination capacity was around 66.4 million m<sup>3</sup>/d and it is expected to witness over 50% increase of this capacity by 2015. This trend would perhaps continue if the world must meet up with increasing demand for water.

Reverse osmosis (RO) is the most commonly used desalination technology worldwide primarily due to its lower cost and simplicity [1, 3 and 4]. However, rejection of low molecular weight substances such as boron remains one of its challenges. This may poses limitations to the application of water from desalination. Though, boron requirement varies across different sector and region of the world [5]. For drinking water, according world health organization (WHO) boron concentration of 2.4mg/L was recently adopted [6]. Study has shown that a typical RO permeate has boron concentration between 0.5-1.2mg/L [7]. For irrigation water, this concentration is high and would have negative impact on the crops

that are sensitive to boron [7, 8]. Therefore, proper measures must be put in place if the water from desalination plant is to be used for irrigation activities.

Techniques such as one pass with or without pH modification, two pass with pH adjustment, and boron selective resins (BSR) are used to lower the boron concentration in RO permeate. However, these methods are associated with additional cost [5]. Although, hybrid systems for boron removal are under way with promising potentials [5]. Further understanding of the exiting approaches especially in the case of BSR without pH adjustment is necessary for sustainability.

Boron selective ion exchange resins are available from different manufacturer but all are made from cross linked macroporous polystyrene with N-methyl-D-glucamine as functional group which comprise of tertiary amine and polyol ends [9]. The removal of boron from solution by these resins follow complexation reaction as presented in equation (1) and (2).



Removal of boron from desalination has been studied using BSR for example Amberlite™ PIWA10 and IRA743, Diaion CRB01 and CRB02, Dewex™ BSR-1 and Purolite<sup>R</sup> and S108 [5, 10, 11, 12, 13]. However, comparative studies between BSRs under the same experimental conditions are rarely carried out.

The objective of this study was to carryout comparative performance of boron removal from seawater reverse osmosis permeate using commercially available boron-selective ion exchange resins, Purolite<sup>R</sup> S110 and S108

## Methodology

This study involved laboratory bench scale experiment with Purolite<sup>R</sup> S108 and S110. All the reagents used were analytical grade supplied by Fisher Scientific, United Kingdom. Each

resin sample was pretreated by soaking in deionized water for about 1440 min and then immersed in 2M NaOH solution for another period of 1440 min at room temperature. It was later rinsed with deionized water until pH of the water wash reached between 7.0-7.5. This process is to establish OH group in the resin. The material was further dried in an oven at temperature of about 40°C for another 2880 min [14]

Azomethine-H reagent was used for determination of boron. The reagent was prepared by dissolving 0.5g Azomethine-H and 1g of ascorbic acid in 50mL of distilled water and transferred to a plastic bottle. Buffer solution was made by dissolving 50g of ammonium acetate in 100mL of distilled water followed by addition of 25mL of glacial acetic acid and 1.4g of ethylenediaminetetraacetic acid (EDTA) disodium salt [14]

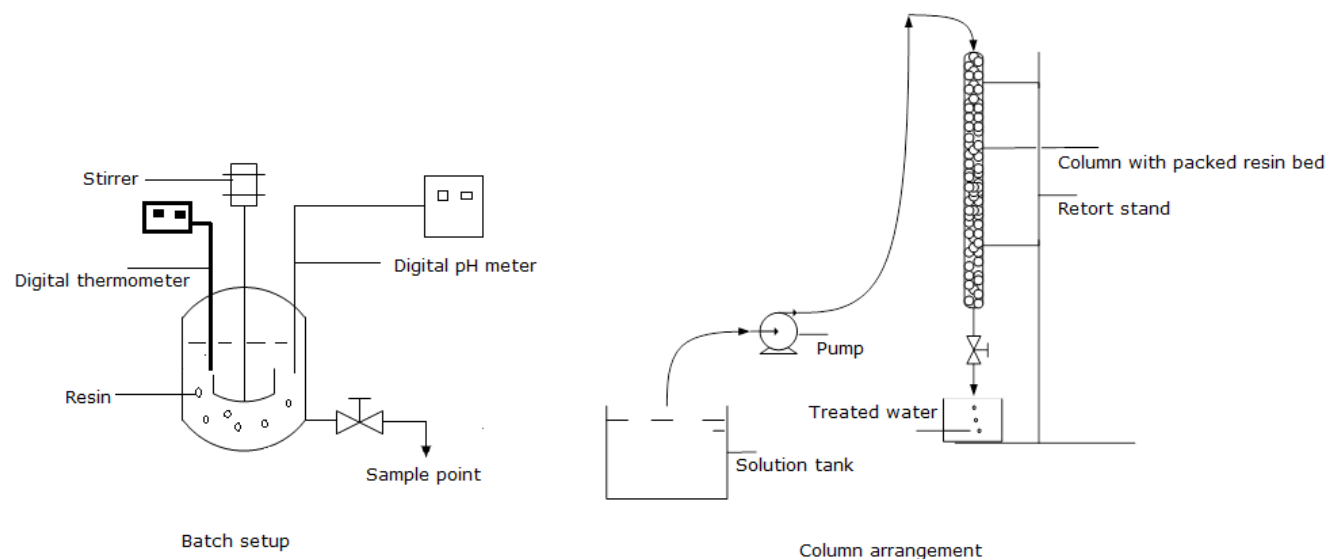
Various boron solutions were prepared from boron standard solution of 1000ppm to mimic the concentration of boron in desalinated water. Samples prepared for analysis were treated as follows. 2.5mL of buffer solution was added to 10mL of the sample followed by 2.5mL of azomethine-H reagent in a plastic bottle and stored in a dark space for a period of 40minutes. UV-Vis CECIL CE 1021, 1000 series spectrophotometer was calibrated according to the manufacturer's manual and used to determine absorbance at a wavelength of 415nm with 10mm 100-Qs cell [14].

In order to study the behavior of different resins in terms of boron removal efficiency and the kinetics, experiment was conducted with S110 (500-700 $\mu$ m) and S108 (425-630 $\mu$ m) in batch and continuous modes. The batch study was carried out with both resins under the same operating conditions of solid-liquid ratio of 1.0g/200mL, initial boron concentration of 5ppm at 350rpm stirring speed, temperature 300K under a constant pH of 9.32 in two separate reactors. After every 20 min, samples were withdrawn and analyzed. This condition has been established elsewhere in our earlier studies [15]. The continuous mode of the experiment was performed in a plastic column of 8mm internal diameter packed with

4mL wet resin. The experiment was first performed with S110 to investigate effect of flow rate under a constant resin bed, temperature and boron concentration to establish optimum condition. Boron solution with initial concentration of 7ppm was administered across the bed in down ward flow using Masterflex economy drive variable speed peristaltic pump VFP002. Flow rate of 3mL/min, 6mL/min and 9mL/min were investigated. The pH and temperature of the solution were maintained at 9.32 and 300K respectively. After every 20 min, sample was collected and analyzed. Optimum flow rate from this investigation was then used for S108 with other parameters remain same as above. Table 1 gives the summary of the experimental parameters. Schematic experimental diagram is shown in Figure 1.

**Table 1:** Experimental parameters

<b>Operation</b>	<b>Parameter</b>	<b>Value</b>
<b>Batch</b>	Mass of resin per volume of solution (g/mL)	1.0/200
	Boron concentration(ppm)	5
	Stirring speed (rpm)	350
	pH	9.32
	Temperature (K)	300
<b>Column</b>	Resin bed (mL)	4
	Boron concentration (ppm)	7
	Temperature (K)	300
	pH	9.32
	Liquid (boron solution) flow rate (mL/min)	3, 6, 9

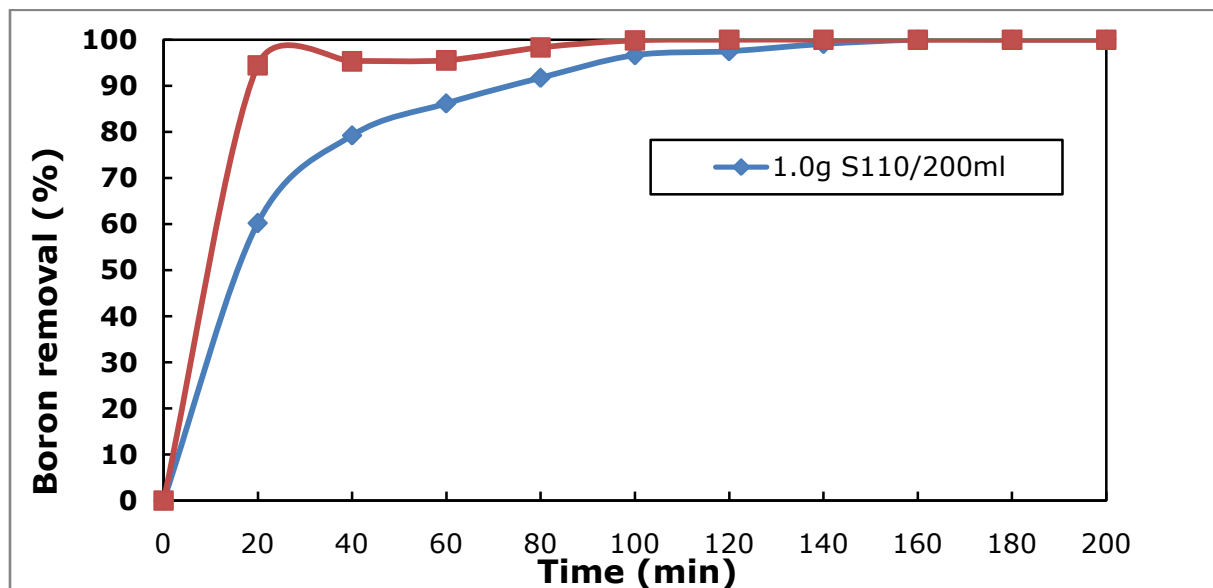


**Figure 1:** Batch and column experimental setup

## Discussion of Results

### Batch study

From the results obtained as presented in Figure 1, over 94% boron removal was recorded with S108 within the first 60 min compared to S110 with about 86% removal. This high performance of S108 is not surprising since it is made of smaller particle size which is an important process parameter. This observation is also in good agreement with studies conducted by Kabay *et al.* 2007 [12]; Yilmaz-Ipek *et al.* 2011 [19]. Generally, the smaller the size of the particle the more boron removal will be achieved due to increased surface area. It is also clear that time required to reach the irrigation requirement of less than 1ppm boron level was less with S108 compared to S110. Furthermore, when large volume of treated water is to be required for massive irrigation system, S108 can be substituted with S110 to reduce the holding time. S108 present a prospect of having a sorption process combined with membrane which can be carried out continuously to give high boron removal within short time.



**Figure 2:** Performance comparison of boron removal between S110 and S108

Kinetic performances of the two resins were carried out. The boron sorption process was fitted to both Lagergren pseudo-first and pseudo-second order models [16, 17]. The result of analysis in both cases followed pseudo-second order kinetics. Table 2 gives the summary of the kinetic parameters. From the slope and intercept of second order model, equilibrium sorption  $q_e$  (mg/g) and initial sorption rate  $r_{sorp} = k_2 q_e^2$  (mg/g.min) can be calculated which in this case were found to be 1.0mg/g, 0.074mg/g.min and 1.0mg/g, 0.459mg/g.min for S110 and S108 correspondingly. The value of equilibrium sorption for both cases tally with the total amount of boron in the system which indicates almost all the boron in the water sample was removed by each of the resins. The initial sorption rate is the sorption at a time  $t$  infinitesimally greater than zero. This value for S110 is less than that of S108 which further justifies that the sorption with S108 can be carried out with less holding time compared to S110 due to improved surface area.

Process kinetics was also studied. Data were also fitted to shrinking core model (SCM) [18] since the boron removal process is a non-catalytic one and the resin is surrounded with aqueous solution which undergoes progressive conversion without altering its integrity.

Also, the kinetic parameters are shown in Table 2. Chemical reaction step was found to be the rate determining for S110 resin which indicates that rate of mass transfer and film diffusion occurred rapidly. Thus, the time for conversion is directly proportional to the radius of the particles. This provides good design information as one can establish the time it will take for the resin to get saturated before regeneration. From the slope, time for complete conversion was 233 min. The value of intercept connotes instantaneous chemical reaction rate at infinitesimal time. For S108 resin, the process was limited by both mass transfer and film diffusion steps but more predominant by film diffusion, therefore the time for conversion is directly proportional to the square of radius of the particles. It shows that rate of chemical reaction at core surface occurred rapidly and the process was limited by the rate of diffusion of boron through the reacted layer. The time for complete conversion of S108 from the slope was found to be 161 min which confirms that S108 process can be carried out within short period of time compared to S110. The intercept signifies the first rate of film diffusion at a time slightly greater than zero.

**Table 2:** Summary of kinetic parameters of batch study

Kinetic Model	S110 (500-700 $\mu$ m)			S108 (425-630 $\mu$ m)		
	Slope	Intercept	R <sup>2</sup>	Slope	Intercept	R <sup>2</sup>
<b>Lagergren Model</b>						
Pseudo-first order	-0.0394	0.2956	0.8949	-0.0415	-1.4389	0.7421
Pseudo-second order	0.9217	13.473	0.9995	0.987	2.1803	0.9999
<b>Shrinking core model (SCM)</b>						
<b>Rate controlling step</b>						
Mass transfer	0.0021	0.6895	0.7595	0.0006	0.9278	0.9284
Film diffusion	0.0136	0.9122	0.8526	0.0062	2.2715	0.9296
Chemical reaction	0.0043	0.2105	0.9902	0.0039	0.4797	0.8878

**Column experiment**

Data from column investigation with S110 was used to develop a breakthrough curve (Figure 3). Increasing the flow rate reduced the boron removal. This is more pronounced



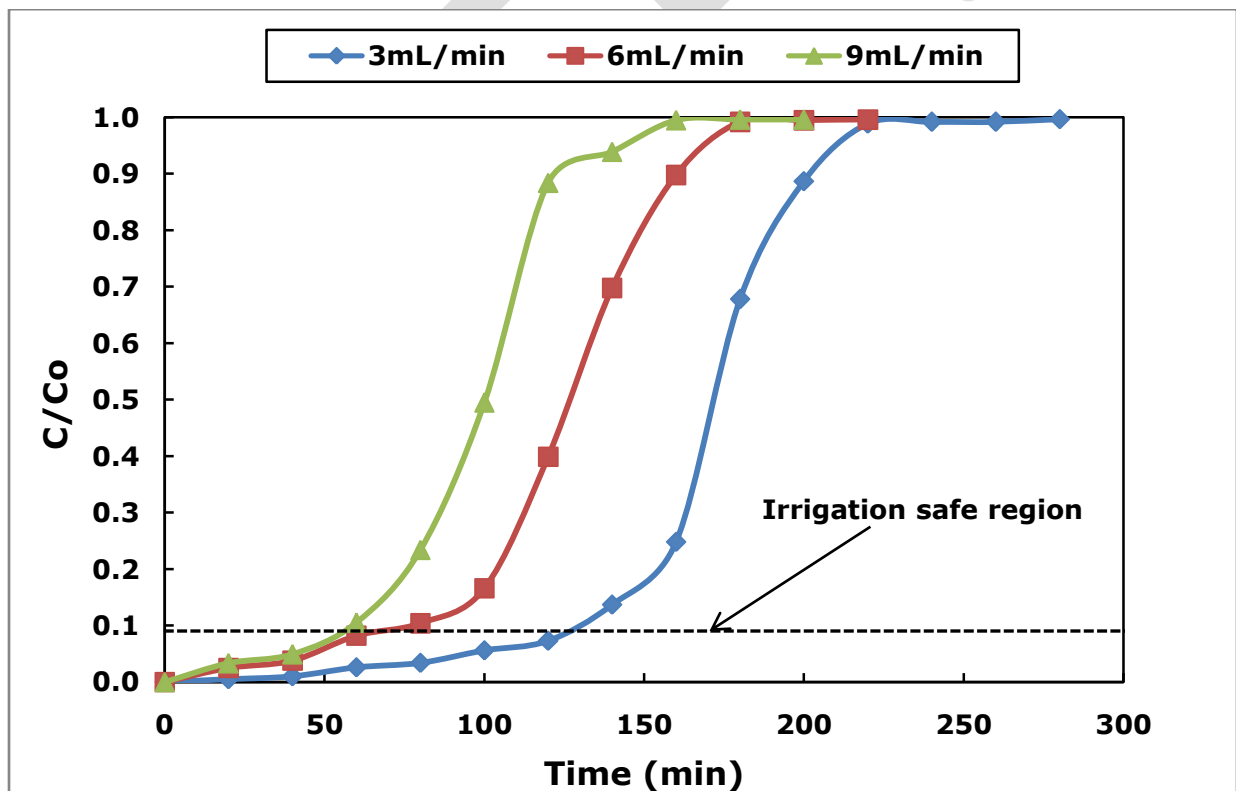
when flow rate was increased from 3ml/min to 6ml/min. It shows that liquid residence time is an important factor during column operation. To attain irrigation water requirement of less than 1ppm boron, the process needed to remove around 90% initial concentration as indicated in the graph. The working period within the irrigation safe region decreased with increasing flow rate. In practical terms, the process with more inflow would have short service life which calls for rapid regeneration. Hence it important to examine the process critically so as to accurately determine the breakthrough for safe boron discharge. In order to compare the performance of the two resins in column studies, flow rate 6mL/min was used with S108 under same condition as above. From Figure 4 below, the service life of S110 is 80min. This far below that of S108 which has working period of 125min. the process kinetics was established (Figure 5) according to Yoon-Nelson model (equation 3). This is a descriptive equation developed based on assumptions of fraction of adsorbate captured and the fraction remaining in the solution that passes through the adsorbent bed. For boron removal, the rate of decrease in fraction of boron captured is directly proportional to the fraction of boron captured and the fraction that passes through the resin bed.

$$t = \tau + \frac{1}{k} \ln \left[ \frac{C}{C_o - C} \right] \quad \text{-----3} \quad [20]$$

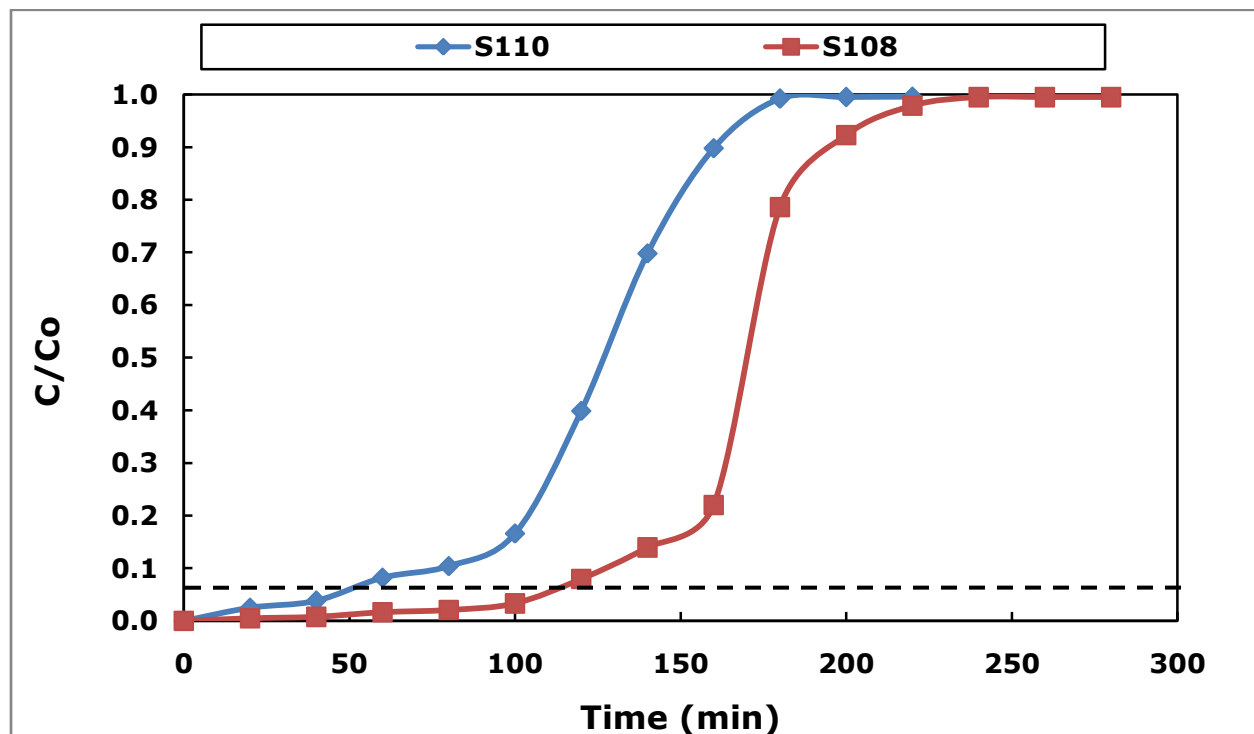
Where  $\tau$  is the time required for the concentration in the effluent to be equal to half the influent concentration,  $t$  is the breakthrough time and  $k$  is the first order rate constant. A straight line plot will give a slope and intercept corresponding to value of  $k^{-1}$  and  $\tau$  respectively. The value of  $\tau$  can also obtained by substituting  $C$  with  $1/2C_o$  in the square bracket. In addition, column capacity ( $W_c$ ) in mg/L is established based on the 50% value of  $\tau$ , influent boron concentration and the solution flow rate ( $\text{mL}/\text{mL}_{\text{resin}} \cdot \text{min}$ ) as given in equation 4.

$$W_e = \frac{1}{2} C_o \times v \times [2\tau] = C_o v \tau \text{-----4} \quad [21]$$

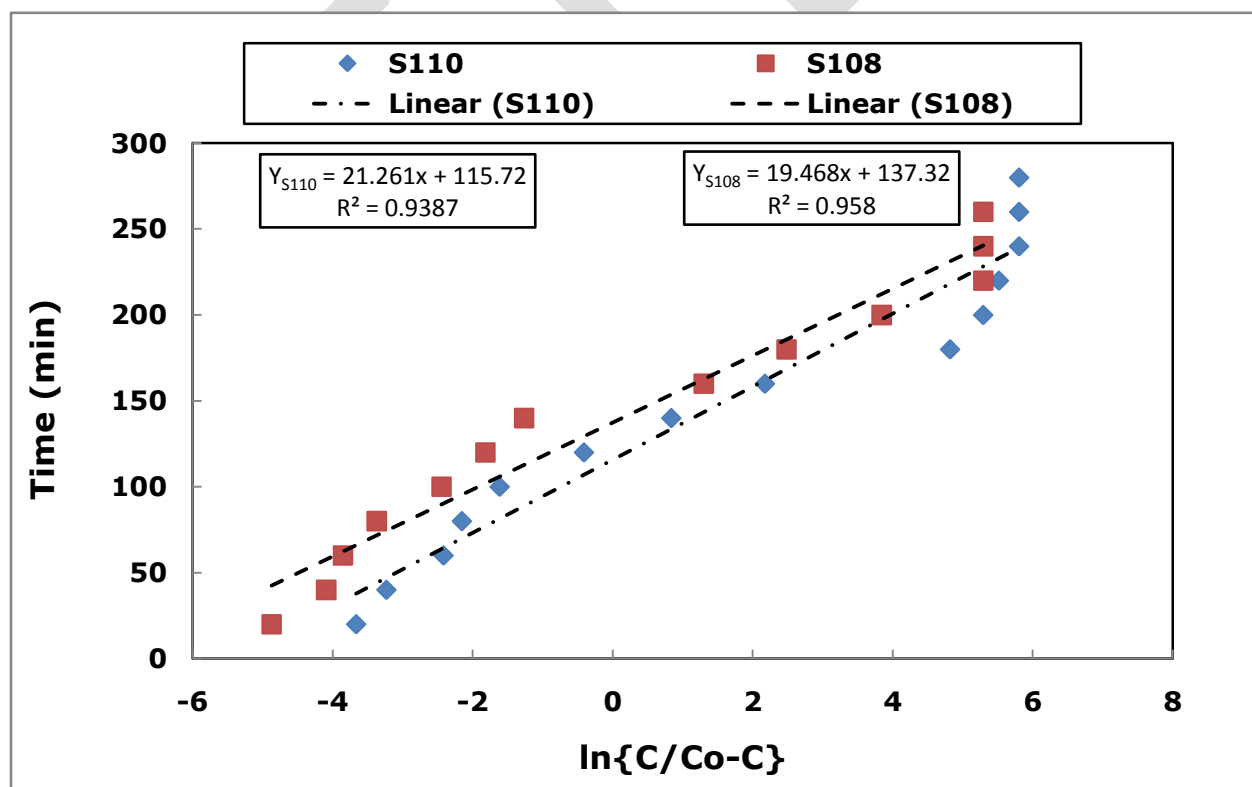
The kinetic parameter and column adsorption capacity is presented in Table 3 below. About 1.215g B/L (0.34eq/L) was adsorbed in the process with S110 while around 1.442g B/L (0.40eq/L) was recorded with S108. More boron was adsorbed with S108 and therefore has better performance compared to S110 resin. However, the capacity of the individual resin falls below the specified capacity given by the manufacturer (0.8 eq/L and 0.6 eq/L for S110 and S108 respectively) [22]. This could be a result of non-proper liquid distribution and less contact time between the liquid and solid in the column. Although these specifications are based on certain flow conditions which differs from our working flow condition.



**Figure 3:** Breakthrough curves of S110 at different flow rate



**Figure 4:** Breakthrough curves of S110 and S108 at flow rate of 6mL/min



**Figure 5:** Plot of t against  $\ln\{C/Co-C\}$  for S110 and S108 at 6mL/min flow rate

**Table 3:** Kinetic parameters of column study

Resin	$\tau$ (min)	$k(\text{min}^{-1})$	Column adsorption capacity (Wc)		
			mg B/mL <sub>resin</sub>	g B/L <sub>resin</sub>	eq/L
S110	115.72	0.0470	1.215	1.215	0.34
S108	137.32	0.0514	1.442	1.442	0.40

### Conclusion

A comparative investigation of boron removal from reverse osmosis permeate was carried out in batch and column operations using Purolite<sup>R</sup> S110 and S108 resins under the same optimum operating conditions. In both studies, the performances of S108 were better than that of S110. This characteristic of S108 is as a result of improved surface area as it was made of smaller particle size. Batch sorption kinetics of both resins followed Lagergren pseudo second order kinetic. When shrinking core model (SCM) was used, chemical reaction was found to be the rate limiting step for S110 while film diffusion controlled S108 process. Column sorption was performed under flow rate of 6mL/min and resin bed of 4mL. The data were fitted to Yoon-Nelson model and the column capacity was found to be 0.34eq/L and 0.40eq/L for process with S110 and S108 respectively.

### Acknowledgements

The authors are thankful to the Federal Government of Nigeria for the funding this project. Thanks also to the Department of Chemical and Environmental Engineering of the University of Nottingham for the supports during this study.

### References

- [1] B. Peñate, L. García-Rodríguez, "Current trends and future prospects in the design of seawater reverse osmosis desalination technology" *Desalination* 284 (2012) 1–8
- [2] Global Water Intelligence (GWI) "The Big Dipper: Contracted Desalination Capacity Forecast-Chart" 10 (1) (2009)

- [3] A. D. Khawaji, I. K. Kutubkhanah, J-M. Wie, "Advances in seawater desalination technologies" *Desalination* 221 (2008) 47-69
- [4] E. Yavuz, Ö. Arar, Ü. Yüksel, M. Yüksel, N. Kabay, Removal of boron from geothermal water by RO System-III-Utilization of SWRO system. *Desalination* 310 (2013) 140-144
- [5] N. Hilal, G. J. Kim, C. Somerfield, "Boron removal from saline water: A comprehensive review." *Desalination* 273(1) (2011) 23-35.
- [6] WHO (2009) Boron in drinking water
- [7] B.V. Lenntech Water Treatment Solutions at: <http://www.lenntech.com/applications/irrigation/quality/irrigation-water-quality.htm> accessed 1st April, 2014
- [8] S. R. Grattan, "Irrigation Water Salinity and Crop Production" *Univ. of Calif. Agric. and Nat. Resour.* 8066 (2002) 9-10
- [9] F. Soto and E. M. Camacho (2005) Boron removal from industrial wastewaters by ion exchange: an analytical control parameter" *Desalination* 181 207- 216
- [10] C. Jacob, Boron removal by ion exchange technology: Seawater desalination. *Desalination* 205 (2007) 47-52
- [11] N. Kabay, S. Sarp, M. Yuksel, M. Kitis, H. Koseog lu, Ö. Arar, M. Bryjak, R. Semiat, Removal of boron from SWRO permeate by boron selective ion exchange resins containing *N*-methyl glucamine groups. *Desalination* 223 (2008) 49-56
- [12] N. Kabay, S. Sarp, M. Yuksel, O. Arar, M. Bryjak, Removal of boron from seawater by selective ion exchange resins. *Reactive & Functional Polymers* 67 (2007) 1643-1650
- [13] N. Kabaya, I. Yilmaz, S. Yamac, S. Samaty, M. Yuksel, U. Yuksel, M. Arda, M. Saglam, T. Iwanaga, K. Hirowatari, Removal and recovery of boron from geothermalwastewater by selective ion exchange resins.I. Laboratory tests. *Reactive & Functional Polymers* 60 (2004) 163-170
- [14] Y. I. Mohammed, K. Garba, and S. Umar, "Analytical Determination of Boron in Irrigation Water Using Azomethine-H: Spectrophotometry" *IOSR Journal of applied chemistry* 7(3) (2014) 47-51
- [15] I. Y. Mohammed, K. Garba, & U. D. Sule, (2014). Reduction of boron level in desalinated water using ion exchange resin: batch studies. *Journal of Emerging Trends in Engineering and Applied Sciences*, 5(3), 179-187.
- [16] Y. S. Ho, "Removal of copper ions from aqueous solution by tree fern." *Water Res.* 37 (10) (2003) 2323-2330
- [17] Y. S. Ho, and G. McKay, Sorption of dye from aqueous solution by peat. *Chem. Eng. J.* 70 (2) (1998) 115-124
- [18] R. W. Missen, C. A. Mims, B. A. Saville, *Introduction to Chemical Reaction Engineering and Kinetics*, John Willey & Sons (1999) pp 229-234

- [19] I. Yilmaz-Ipek, N. Kabay, A. R. Ozdural, Non-equilibrium sorption modeling for boron removal from geothermal water using sorption-microfiltration hybrid method. *Chemical Engineering and Processing* 50 (2011) 599– 607
- [20] Yoon, Y.H., Nelson, J.H., (1992) Breakthrough Time and Adsorption Capacity of Respirator Cartridges, *American Industrial Hygiene Association Journal*, 53:303-316
- [21] Aksu, Z., Onen, F. G., (2004) Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves, *Process Biochem.* 39 599–613
- [22] Purolite Engineering bulletin. Accessed January 2014 at [http://purolite.com/Customized/CustomizedControls/Products/Resources/rid\\_891.pdf](http://purolite.com/Customized/CustomizedControls/Products/Resources/rid_891.pdf)