Removal of Boron by Surfactant Modified Zeolitic Tuff from Northeastern Greece

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Abstract

Boron adsorption on surfactant modified zeolite (SMZ) was investigated, in the perspective of using SMZ for B removal from irrigation waters, since SMZ has been proven efficient adsorbent for many anions. A calcareous clinoptilolite was used and a sub-sample was treated with HCl. Then the charge of the external surface of the untreated and treated zeolite was modified and B adsorption was studied. The SMZ adsorbed B and its adsorption capacity was increased with HCl treatment and pH adjustment at the strongly alkaline range. However, in all cases the relative amounts of B removed from solution were much lower than other anions reported in the literature. In addition, B concentration in the equilibrium solution was above 3 mg L^{-1}, which is considered a critical limit for B in irrigation waters in respect to the risk of B phytotoxicity. It was concluded that SMZ is not an effective means for B removal from irrigation waters and thus its use for B water treatment is not recommended.

Keywords: boron adsorption; irrigation waters; surfactant modified zeolite

Abbreviations: surfactant modified zeolite (SMZ); cation exchange capacity (CEC)

1. Introduction

High B concentration in irrigation water can lead to B accumulation in soils causing phytotoxicity. Consequently, B concentration in water is one of the parameters that determine the suitability of water for irrigation (Nable et al., 1997). In general, B concentrations in irrigation water higher than 3 mg L^{-1} can cause adverse effects on most crops (FAO, 1985). Specifically, according to Scofield (1936) the permissible B concentration in irrigation water is ≤ 1 mg L^{-1} for sensitive crops, ≤ 2 mg L^{-1} for semi-tolerant crops and ≤ 3 mg L^{-1} for tolerant crops. Furthermore, according to Keren and Bingham (1985) the permissible B concentration ranges in irrigation water are 0.3 to 1 mg L^{-1} for sensitive crops, 1 to 2 mg L^{-1} for semi-tolerant crops and 2 to 4 mg L^{-1} for tolerant crops. Several studies concerning treatments of water to reduce B concentration are reported in the literature which include chemical methods, such as the adsorption using adsorbents like lime, alum, ferric salts (Waggot, 1969) and compounds of Ca, Mg and Na (Dionisiou et al., 2006; Okay et al., 1985), precipitation, membrane filtration, reverse osmosis, use of B selective resins and use of aquatic plants (Chieng & Chong, 2012). Among the previously mentioned methods, adsorption is attracting more attention, due to its simplicity and low cost (Ozturk & Kavak, 2005).

Zeolite is a porous alumino-silicate mineral, with high adsorption capacity for cations, because of its high negative charge and consequently its high cation exchange capacity (CEC) (Ming & Mumpton, 1989). SMZ, i.e. zeolite with positive surface charge after its surface modification with a surfactant substance, has been proven effective adsorbent for many anions, such as NO_3^-, SO_4^{2-} (Li et al., 1998), CrO_4^{2-} (Haggerty & Bowman, 1994; Li, 2004), $H_2AsO_4^-$ and $HAsO_4^{2-}$ (Li et al., 2007), ClO_4^- (Zhang et al., 2007), $HSeO_3^-$ and SeO_4^{2-} (Frenay et al., 2000). Since SMZ has been proven an effective adsorbent for many anions it could be also useful for removing B from water through adsorption. However, studies concerning B adsorption on the SMZ are rare in the literature (Demircivi & Nasun-Saygili, 2010).

The objectives of this study were to initially investigate B adsorption on a SMZ, under different conditions of zeolite's pretreatment, prior its surface modification, and of pH and B concentration in the external solution, in the perspective of using this material for B removal from irrigation waters.

2. Materials and Methods

2.1 Pretreatment and Surface Modification of the Zeolite

The zeolite used was a clinoptilolite with the chemical formula $(Ca_{1.5}K_{1.4}Mg_{0.6}Na_{0.5})$ $(Al_{6.2}Si_{29.8}O_{72})\cdot20H_2O$, obtained from the Greek region Petrota, a village of the prefecture of Evros in Greece (Filippidis, 2010; Filippidis & Kantiranis, 2007) and its chemical composition, as it was determined by the Department of Mineralogy-Petrology-Economic Geology of the Aristotle University of Thessaloniki, using X-ray diffraction analysis is presented in Table 1. The zeolite was sieved through a 2 mm sieve and this material was used for all analyses and B adsorption experiments, after its pretreatment and modification of the surface charge. The total and the external CEC of the zeolite were determined employing the method of Ming and Dixon (1987) and were 226 and 10 $cmol_c\,kg^{-1}$, respectively (Table 1).

Certain quantity of the natural zeolite was treated with 1 M HCl once, to improve its subsequent surface modification and thus to increase its adsorbing capacity for B. Specifically, a quantity of the zeolite, sufficient to conduct the following experiments, was equilibrated with 1 M HCl, at a ratio 1 / 20 (w / v), initially for 2 h, at $60 \pm 1\,°C$ and then for 24 h, at $25 \pm 1\,°C$, with intermittent shaking. Then, the zeolite was washed with distilled water and dried at $100 \pm 1\,°C$.

The modification of the surface charge of the untreated and treated zeolite was accomplished using hexadecyltrimethylammonium bromide ($C_{19}H_{42}BrN$ or HDTA-Br), according to Bowman et al. (2000). Specifically, a quantity of the untreated and treated zeolite, sufficient to conduct all the B adsorption experiments, was equilibrated with 0.05 M HDTMA-Br, at a ratio 1 / 4 (w / v), for 24 h, at $25 \pm 1\,°C$, with intermittent shaking. The solution of the 0.05 M HDTMA-Br was added to the zeolite at an amount of the HDTMA-Br equivalent to twice the external CEC of the zeolite. At the end of the equilibration time, the SMZ was washed with distilled water and air-dried.

Table 1. Certain chemical properties of the natural zeolite

Cation Exchange Capacity ($cmol_c\,kg^{-1}$)	226
External Cation Exchange Capacity ($cmol_c\,kg^{-1}$)	10
SiO_2 ($g\,kg^{-1}$)[†]	679
H_2O ($g\,kg^{-1}$)[†]	131
Al_2O_3 ($g\,kg^{-1}$)[†]	120
CaO ($g\,kg^{-1}$)[†]	31
K_2O ($g\,kg^{-1}$)[†]	25
MgO ($g\,kg^{-1}$)[†]	8.9
Na_2O ($g\,kg^{-1}$)[†]	5.1
TiO_2 ($g\,kg^{-1}$)[†]	< 0.1
Fe_2O_3 ($g\,kg^{-1}$)[†]	< 0.1
MnO ($g\,kg^{-1}$)[†]	< 0.1
Si/Al [†]	4.8

[†] The chemical composition of the zeolite was determined by the Department of Mineralogy-Petrology-Economic Geology of the Aristotle University of Thessaloniki.

2.2 Boron Adsorption Experiments

Initially, B adsorption experiments were conducted employing the natural zeolite, without any treatment or surface charge modification. However, the results showed that the amounts of the B adsorbed on the natural zeolite were negligible (data not shown). Thus, only the B adsorption experiments on the SMZ (untreated and treated) are described below and their results are presented in the subsequent section.

Boron adsorption data were obtained by a slight modification of the technique used by Li et al. (2007), at two pH values, namely 7.0 ± 0.1 and 9.5 ± 0.1 for the untreated SMZ and 3.0 ± 0.1 and 9.5 ± 0.1 for the treated SMZ. Specifically, five g sub-samples of the SMZ (untreated or treated), in two replications, were placed in polypropylene centrifuge tubes with 20 mL of deionized water containing B at concentrations 0, 5, 10 and 15 mg L^{-1}, as H_3BO_3. The suspensions were equilibrated for 24 h, at 25 ± 1 °C, with intermittent shaking. At the end of the equilibration period the tubes were centrifuged and the supernatant liquid was filtered and analyzed for B by the azomethine-H method (John et al., 1975), using a UV-Vis spectrometer (Lambda 5, Perkin-Elmer). Adsorbed B was calculated as the difference between the amount added and that found in solution at equilibrium.

For the amounts of adsorbed B, within each B concentration in the external solution, analysis of variance (ANOVA) was conducted and LSD test was used for mean comparisons.

3. Results and Discussion

The amounts of B adsorbed on the untreated SMZ at the alkaline pH were significantly higher than the amounts of B adsorbed at the neutral pH, in all cases of the initial B concentration in the external solution studied (Table 2). Less than 17 % of the added B was removed by the SMZ when the pH of the equilibrium solution was 7.0 ± 0.1, whereas 24 % of the added B was removed at pH 9.5 ± 0.1.

It is well known that B exists in solution with two chemical forms mainly, i.e. boric acid (H_3BO_3) and borates anions [$B(OH)_4^-$], and the proportion of these two forms is pH depended. Since pKa of H_3BO_3 is 9.24, H_3BO_3 is the dominant B chemical species at acidic and neutral pH, whereas as pH increases to the alkaline range, $B(OH)_4^-$ are increased at appreciable amounts and become the dominant B chemical species at the strongly alkaline pH range (pH = 9.24) (Goldberg, 1993).

According to Li and Bowman (1997) the anion adsorption mechanism on SMZ (with HDTMA-Br) is anion exchange, meaning the anions are exchanged for Br^- originating from the HDTMA-Br on the surface of the zeolite and held by electrostatic bond. Based on the above, the lower amounts of B adsorbed on the untreated SMZ at pH 7.0 ± 0.1 compared to the amounts adsorbed at pH 9.5 ± 0.1, could be attributed to the different B chemical species. Apparently, the SMZ exhibited lower affinity for the neutral H_3BO_3, which is the dominant B chemical species at a neutral pH value, than the univalent $B(OH)_4^-$, which is the dominant B chemical species at the strongly alkaline pH range.

Similarly to the untreated SMZ, the amounts of B adsorbed on the treated SMZ at the alkaline pH were significantly higher than the amounts of B adsorbed at the acidic pH, in all cases of the initial B concentration in the external solution studied (Table 2). Less than 16 % of the added B was removed by the SMZ when the pH of the equilibrium solution was 3.0 ± 0.1, whereas 14-47 % of the added B (depending on the initial B concentration in the external solution) was removed at pH 9.5 ± 0.1. Moreover, at the alkaline pH value, the amounts of B adsorbed on the treated SMZ were significantly higher than the untreated SMZ, in almost all cases (Table 2). This was an indication that the acid treatment of the zeolite prior its surface charge modification increased SMZ's adsorption capacity for $B(OH)_4^-$, which is the predominant B species at a such alkaline pH value.

Although the SMZ (untreated or treated) adsorbed B, the relative amounts of B adsorbed were much lower than other anions reported in the literature. Specifically, several studies indicated that SMZ is an effective adsorbent for many anions, such as SO_4^{2-} with an adsorption percentage of 90-100 % (Li, 2003; Li et al., 1998), CrO_4^{2-} with an adsorption percentage of 90-100 % (Haggerty & Bowman, 1994; Li, 2004) and $H_2AsO_4^-$ and $HAsO_4^{2-}$ with an adsorption percentage higher than 90 % (Sullivan et al., 2003).

Furthermore, the SMZ's capacity to adsorb B was much lower than other B adsorbents reported in the literature. Such materials are, ferromagnesian minerals and magnesium hydroxide (Rhoades et al., 1970), hydrous oxides and iron aluminium (McPhail et al., 1972), allophane (Su & Suarez, 1997), montmorilonite, illite and kaolinite (Chieng & Chong, 2012; Keren & O' Connor, 1982), humic acids (Gu & Lowe, 1990), fly ash and coal (Polat et al., 2004), magnesia (Dionisiou et al., 2006), activated carbon (Kluczka et al., 2007) and selective resins as Amberlite IRA-743 (Demircivi & Nasun-Saygili, 2008).

In addition, in all cases of the initial B concentration in the external solution, B in the equilibrium solution was ranged from 3.8 ± 0.2 to 12.6 ± 0.3 mg L^{-1}, meaning it was higher than the value of 3 mg B L^{-1}, which is considered a critical limit for B in irrigation waters, since B concentrations higher than this value are expected to have undesirable effects on most crops, according to Scofield (1936), Keren and Bingham (1985) and FAO (1985).

Table 2. Boron adsorbed (mg kg^{-1}) on the untreated or treated SMZ, at the different pH values and B concentrations in the external solution

pH	B initial (mg L^{-1})		
	5	10	15
	Untreated SMZ		
7.0 ± 0.1	2.2[†] ± 0.4[‡] b[*]	3.4 ± 0.4 c	10.0 ± 0.4 c
9.5 ± 0.1	4.7 ± 0.7 a	9.9 ± 0.4 b	15.0 ± 0.3 b
	Treated SMZ		
3.0 ± 0.1	0.37 ± 0.0 c	1.6 ± 0.4 d	9.5 ± 1.1 c
9.5 ± 0.1	2.7 ± 0.4 b	13.3 ± 0.1 a	28.1 ± 0.1 a

[†] Mean.

[‡] Standard error.

[*] Values followed by different letter, within the same column, are significantly different, at $p \leq 0.05$, using the LSD test.

4. Conclusion

In conclusion, the SMZ adsorbed B and its adsorption capacity increased with pH increase and treatment with HCl (before its surface modification). However, in all cases, the relative amounts of B adsorbed on the SMZ were low compared to the amounts of other anions adsorbed on the same material or to B amounts adsorbed on other materials. Furthermore, B concentration in the equilibrium solution was above the critical limit of 3 mg L^{-1} for irrigation waters. Consequently, it seemed that SMZ is not an effective means for B removal from irrigation waters; therefore its use for water treatment in respect to B is not recommended.

References

Bowman R. S., Sullivan, Z., & Li, Z. (2000). Uptake of cations, anions and nonpolar organic molecules by surfactant modified clinoptilolite rich tuff. In C. Collela, & A. Mumpton (Eds.), *Natural zeolites for the third millennium*. Napoli, Italy: De Frede.

Chieng, H. J., & Chong, M. F. (2012) .A review on boron adsorption using various adsorbents. *Global Journal of Environmental Science and Technology, 2*, 1-14.

Demircivi, P., & Nasun-Saygili, G. (2008). Removal of boron from waste waters by ion-exchange in a batch system. *WASET, 47*, 95-98.

Demircivi, P., & Nasun-Saygili, G. (2010). Removal of boron from waste waters using HDTMA-modified zeolites, *Proceedings of the 11th Conference on Environmental Science and Technology, September 3-5-2010 Chania, Greece*.

Dionisiou, N., Matsi, T., & Misopolinos, N. D. (2006). Use of Magnesia for B Removal from Irrigation Waters. *Journal of Environmental Quality, 35*(6), 2222-2228. http://dx.doi.org/10.2134/jeq2006.0093

FAO. (1985). *Water quality for agriculture*. FAO irrigation and drainage paper 29, Rev. 1. Rome, Italy: FAO.

Filippidis, A. (2010). Environmental, industrial and agricultural applications of Hellenic Natural Zeolite. *Hellenic Journal of Geosciences, 45*, 91-100. Retrieved from http://www.hellenjgeosci.geol.uoa.gr/45/Filippidis.pdf

Filippidis, A., & Kantiranis, N. (2007). Experimental neutralization of lake and stream waters from N. Greece using domestic HEU-type rich natural zeolitic material. *Desalination, 213*(1-3), 47-55. http://dx.doi.org/10.1016/j.desal.2006.03.602

Frenay, J., Lambert, C., & Bastin, D. (2000). Use of surface-modified zeolite to clean industrial effluents containing metal cation and anions. *Public Report for European Research program with acronym METASEP No EVK1-CT-2000-00083, European Union, Brussels*.

Goldberg, S. (1993). Chemistry and mineralogy of boron in soils. In U.C. Gupta (Ed.), *Boron and its role in crop production* (pp. 3-44). Boca Raton, USA: CRC Press.

Gu, B., & Lowe, L. E. (1990). Studies on the adsorption of boron on humic acids. *Canadian Journal of Soil Science, 70*(3), 305-311. http://dx.doi.org/10.4141/cjss90-031

Haggerty, G. M., & Bowman, R. S. (1994). Sorption of chromate and other inorganic anions by organozeolite. *Environmental Science and Technology, 28*(3), 452-458. http://dx.doi.org/10.1021/es00052a017

John, M. K., Chuah, H. H., & Neufeld, J. H. (1975). Application of improved azomethine-H method to the determination of boron in soils and plants. *Analytical Letters, 8*(8), 559-568. http://dx.doi.org/10.1080/00032717508058240

Keren, R., & Bingham, F. T. (1985). Boron in water, soils and plants. *Advances in Soil Science, 1*, 229-276. http://dx.doi.org/10.1007/978-1-4612-5046-3_7

Keren, R., & O'Connor, G. A. (1982). Effect of exchangeable ions and ionic strength on boron adsorption by montmorillonite and illite. *Clays and Clay Minerals, 30*(5), 341-346. http://dx.doi.org/10.1346/CCMN.1982.0300504

Kluczka, J., Trojanowska, J., Zolotajkin, M., Ciba, J., Turek, M., & Dydo, P. (2007). Boron removal from wastewater using adsorbents. *Environmental Technology, 28*(1), 105-113. http://dx.doi.org/10.1080/09593332808618769

Li, Z. (2003). Use of surfactant-modified zeolite as fertilizer carriers to control nitrate release. *Microporous and Mesoporous Materials, 61*(1-3), 181-188. http://dx.doi.org/10.1016/S1387-1811(03)00366-4

Li, Z. (2004). Influence of solution pH and ionic strength on chromate uptake by surfactant-modified zeolite. *Journal of Environmental Engineering, 130*(2), 205-208. http://dx.doi.org/10.1061/(ASCE)0733-9372(2004)130:2(205)

Li, Z., & Bowman, R. (1997). Counterion effects on the sorption of cationic surfactant and chromate on natural clinoptilolite. *Environmental Science and Technology, 31*(8), 2407-2412. http://dx.doi.org/10.1021/es9610693

Li, Z., Anghel, I., & Bowman, R. (1998). Sorption of oxyanions by surfactant-modified zeolite. *Journal of Dispersion Science and Technology, 19*(6-7), 843-857. http://dx.doi.org/10.1080/01932699808913218

Li, Z., Beachner, R., McManama, Z., & Hanlie, H. (2007). Sorption of arsenic by surfactant-modified zeolite and kaolinite. *Microporous and Mesoporous Materials, 105*(3), 291-297. http://dx.doi.org/10.1016/j.micromeso.2007.03.038

McPhail, M., Page, A. L., & Bingham, F. T. (1972). Adsorption interactions of monosilicic and boric acid on hydrous oxides of iron and aluminium. *Soil Science Society of America Proceedings, 36*(3), 510-514. https://www.soils.org/publications/sssaj/pdfs/36/3/SS0360030510

Ming, D. W., & Dixon, J. B. (1987). Quantitative determination of clinoptilolite in soils by a cation-exchange capacity method. *Clays and Clay Minerals, 35*(6), 463-468. http://dx.doi.org/10.1346/CCMN.1987.0350607

Ming, D. W., & Mumpton, F. A. (1989). Zeolites in soils. In J. B. Dixon, & S. Weed (Eds.), *Minerals in soil environments* (SSSA book series 1, 2nd ed., pp. 873-911). Madison, USA: SSSA.

Nable, R. O., Bañuelos, G. S., & Paull, J. G. (1997). Boron toxicity. *Plant Soil, 193*(1-2), 181-198. http://dx.doi.org/10.1023/A:1004272227886

Okay, O., Güclü, H., Soner, E., & Balka, T. (1985). Boron pollution in the Simav river, Turkey and various methods of boron removal. *Water Research, 19*(7), 857-862. http://dx.doi.org/10.1016/0043-1354(85)90143-5

Ozturk, N., & Kavak, D. (2005). Adsorption of boron from aqueous solutions using fly ash: Batch and Column studies. *Journal of Hazardous Materials, 127*(1-3), 81-88. http://dx.doi.org/10.1016/j.jhazmat.2005.06.026

Polat, H., Vengosh, A., Pankratov, I., & Polat, M. (2004). A new methodology for removal of boron from water by coal and fly ash. *Desalinization, 164*(2), 173-188. Retrieved from http://ac.els-cdn.com/S0011916404001766/1-s2.0-S0011916404001766-main.pdf?_tid=4f68b898-2c18-11e3-9c86-00000aab0f26&acdnat=1380797047_6a7292a1582cd5aefd36122c29dc909a

Rhoades, J. D, Ingvalson, R. D., & Hatcher, J. T. (1970). Adsorption of boron by ferromagnesian minerals and magnesium hydroxide. *Soil Science Society of America Proceedings, 34*(6), 938-941. Retrieved from https://www.soils.org/publications/sssaj/pdfs/34/6/SS0340060938

Scofield, C. S. (1936). The salinity in irrigation water. *Inst. Ann. Rpt., 1935*, 275-287.

Su, C., & Suarez, D. L. (1997). Boron sorption and release by allophone. *Soil Science Society of America Journal, 61*(1), 69-77. http://dx.doi.org/10.2136/sssaj1997.03615995006100010012x

Sullivan, E. J., Bowman, R. S., & Legiec, I. A. (2003). Sorption of arsenic from soil-washing leachate by surfactant-modified zeolite. *Journal of Environmental Quality, 32*(6), 2387-2391. http://dx.doi.org/10.2134/jeq2003.2387

Waggott, A. (1969). An investigation of the potential problem of increasing boron concentrations in rivers and water courses. *Water Research, 3*(10), 749-765. http://dx.doi.org/10.1016/0043-1354(69)90039-6

Zhang, P., Avudzega, D., & Bowman, R. S. (2007). Removal of perchlorate from contaminated waters using surfactant-modified zeolite. *Journal of Environmental Quality, 36*(4), 1069-1075. http://dx.doi.org/10.2134/jeq2006.0432

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