Boron adsorption by steelmaking slag for boron removal excess from irrigation (natural and waste) waters

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Abstract

Purpose

Steelmaking slag, a by-product of the steel-refining process, could be used for removing B excess from irrigation natural and waste waters, due to its strongly alkaline reaction. The objectives of this study were to: a) establish the optimum external solution / adsorbent ratio and equilibration time of B adsorption by the slag and b) assess the slag's capacity to adsorb B.

Methods

Two preliminary B adsorption experiments were conducted to determine the optimum external solution / adsorbent ratio and equilibration time. The optimum conditions were employed for the main B adsorption experiment and the non-linear Langmuir and Freundlich isotherms were fitted to the B adsorption data.

Results

Boron adsorption increased with the increase of the external solution / adsorbent ratio up to the ratio of 200:1. Although, almost 40 % of B was adsorbed within the first hour of equilibration period, the adsorption gradually increased until the 72 h. The Langmuir B adsorption maximum was almost 150 mg g^{-1}, considerably higher than other adsorbents, like fly ash, calcite and magnesia. At B initial concentrations lower than 4 mg L^{-1}, slag removed 60 % of B and reduced it below the permissible levels for irrigation waters (< 3 mg L^{-1}) for most crops. The pH of the equilibrium solution was 10.3 ± 0.8 and dropped to acceptable levels for irrigation waters (< 8.5), after contact with atmosphere for one week.

Conclusions

Consequently, steelmaking slag can be used effectively for removing B excess from irrigation waters. However, attention should be given to the pH of the slag-treated waters.

Keywords Adsorption; Boron; Irrigation waters; Steelmaking slag

Introduction

Boron concentration in irrigation (natural and waste) waters higher than 3 mg B L^{-1} can cause adverse effects on most crops [1]. Consequently, it is essential that B excess in irrigation waters should be reduced prior to application. As of now, B removal from water by adsorption not only has been the most cost-effective method but also a method by which even low B concentrations can be removed. Several materials are proposed in the literature as B adsorbents, like chelating resins, activated C, oxides, hydroxides and industrial wastes [2], fly ash and coal [3, 4] and magnesia [5]; certain of them have been proven effective B adsorbents.

Steelmaking slag, a by-product of the steel refining process [6], is mainly a calcareous material with strongly alkaline reaction and contains among others Ca, Mg, Fe and Al oxides at considerable amounts [7]. The slag's reaction and content favor B adsorption [8]. Steelmaking slag had been tested as adsorbent for the removal of metals and non-metals, from natural and waste waters. In the literature is reported removal of Cu, Zn, Cd, Pb and As, from wastewaters by the particular slag, higher than 90 % [9, 10, 11] and removal of P higher than 99 % [12]. As far as B is concerned, percentages of B removal by the slag higher than 95 % are reported [13, 14].

Based on the above, due to its alkaline reaction and composition, steelmaking slag could be used for removing B excess from irrigation waters, through adsorption. The purpose of this work was to investigate extensively B adsorption on steelmaking slag by: a) establishing the optimum external solution / adsorbent ratio and equilibration time of B adsorption and b) assessing the capacity of the slag to adsorb B, by fitting non-linear isotherms to B adsorption data

Materials and Methods

Certain properties of the steelmaking slag

A sample of ground steelmaking slag (EINECS No: 266-004-1 CAS No: 65996-71-6) of particle size fraction < 0.1 mm was obtained from the Greek industry Aeiforos (SIDENOR). The slag's composition was CaO (53.9 %), SiO_2 (18.1 %), FeO (7.9 %), MgO (4.7 %), Al_2O_3 (3.2 %), MnO (2.1 %), Cr (< 0.06 %), Zn (< 0.04 %) and other metals (< 0.02 %) [7]. In the present study, the slag was analyzed for moisture content, pH and EC (in suspension with water at a ratio of 1:2), in five replications. Briefly, the slag had low moisture content (11 ± 8 g kg^{-1}), strongly alkaline reaction (pH 12.1 ± 0.1) and increased EC (7.6 ± 0.2 dS m^{-1}). Moreover, qualitative mineralogical composition of the slag, before and after equilibration with H_2O and drying, was determined by x-ray diffraction patterns of randomly oriented powder specimens.

Boron adsorption experiments

Two preliminary and a main B adsorption experiment on the steelmaking slag were conducted at 25 ± 1 °C, in three replications. For each experiment, after equilibration, pH, EC and B by the azomethine-H method [15] were determined in the equilibrium solution. Adsorbed B was calculated as the difference between the amount added and that found in solution at equilibrium. For all experiments, B solutions of 0-500 mg B L^{-1} as H_3BO_3 were used for equilibration. Ratios of 10:1-500:1 were investigated for the optimum solution / adsorbent ratio determination and periods of 1-72 h were investigated for the optimum equilibration time determination. Optimum solution / adsorbent ratio (200:1) and equilibration time (72 h), which were obtained from the preliminary experiments, were employed for the main B adsorption experiment. In addition, at the end of the main B adsorption experiment, pH was determined every 24 h for the following days in order to ensure that it had dropped below the acceptable levels for irrigation waters (< 8.5) [1].

Statistical analysis

The B adsorption capacity of the slag was determined from the data of the main B adsorption experiment after fitting to them the Langmuir (1) and Freundlich (2) equations by nonlinear regression, using the Levenberg-Marquardt algorithm and the statistical package SPSS, version 25.0. The goodness of fit for both equations was evaluated using the *F*-test.

Langmuir: $x = KMC/(1+KC)$ (1)

Freundlich: $x = kC^n$ (2)

where: x is adsorbed B (mg g^{-1}), C is B in the equilibrium solution (mg L^{-1}) and K, M, k and n are parameters. Specifically, K (L mg^{-1}) express the affinity of the slag for B, M (mg g^{-1}) is the maximum B adsorption capacity of slag, k is the amount of adsorbed B when C = 1, n is a measure of B adsorption intensity.

Results and Discussion

The results of the preliminary B adsorption experiments showed that as the ratio of external solution / adsorbent increased, B adsorption also increased. These results contradict other researchers' findings, since the opposite trend has been observed for other inorganic alkaline materials, which have been tested as B adsorbents [3, 4, 5, 16]. From all ratios, the 200:1 ratio was considered as the optimum one, because at the specific ratio B adsorption seemed to maximize. As far as the optimum equilibration time is concerned, B adsorption seemed to be completed to a large extent at the end of the first hour of the equilibration period, since 38.6 ± 5.7 % of B had been adsorbed. However, a gradual increase in B adsorption was noticed afterwards, while after 72 h of equilibration, 51.1 ± 14.0 % of B was adsorbed. Although the 24 h are considered adequate time for equilibration between solid and liquid phase in B adsorption experiments [8], in the current study the 72 h were considered as the optimum equilibration period, because at the particular time B adsorption seemed to maximize.

Both the Langmuir and Freundlich nonlinear equations were fitted satisfactorily to the B adsorption data (Fig. 1), with the Langmuir equation to be slightly superior to the Freundlich, as this was judged from the values of the *F*-test (Table 1). Langmuir's adsorption maximum (145 mg g^{-1}) (Table 1) indicated that steelmaking slag exhibited high B adsorption capacity, which was considerably higher than that of other adsorbents reported in the literature. Specifically, other researchers reported Langmuir B adsorption maximum 0.17 mg g^{-1} [16] and 0.30 mg g^{-1} [4] for fly ash, 0.215 mg g^{-1} for calcite [17] and 4.45 mg g^{-1} for magnesia [5].

When B concentration in the external solution ranged between 1-4 mg L^{-1}, slag achieved an average B removal of 60 % and reduced B concentration below critical levels for irrigation waters (< 3 mg L^{-1}). The EC of the equilibrium solution had a mean value of 1.6 ± 0.1 dS m^{-1}, which is considered acceptable for irrigation waters for most crops. The pH of the equilibrium solution was strongly alkaline initially (10.3 ± 0.8) and then dropped to acceptable levels for irrigation waters (< 8.4) after being in contact with atmosphere for seven days [1].

The steelmaking slag's high alkaline reaction substantiated its high adsorption capacity for B to a large extent, but further investigation of the slag's mineralogical composition, through x-ray diffraction analysis, was considered essential for better understanding the B adsorption process. These results showed that the slag is mainly an amorphous material (Fig. 2); however, certain crystalline phases can be easily distinguished [$Ca(OH)_2$ and $CaCO_3$]. Crystalline phases which are not identified in Fig. 2 correspond to hydrous Si-Ca phases. It is worth noting that during equilibration with H_2O, the slag's mineralogical composition changed due to $Ca(OH)_2$ transformation to $CaCO_3$ (Fig. 2). Consequently, the slag's high B adsorption capacity could be attributed not only to its strongly alkaline reaction but also to its mineralogical composition and its alteration during the equilibration period of the B adsorption experiment. The findings of the current study are supported by other researchers findings, who reported that B adsorption by amorphous materials is higher than that of the well crystallized materials [18] and that $CaCO_3$ favors B adsorption [17].

Conclusions

According to Langmuir's nonlinear equation, steelmaking slag exhibited an adsorption maximum that reached almost 150 mg g^{-1}, being considerably higher than that of other B adsorbents. Based on its high B adsorption capacity, steelmaking slag can be used effectively for removing B excess from irrigation (natural and waste) waters. However, the pH of slag-treated waters should be considered in the perspective of using them for irrigation purposes.

References

1. Ayers, R. S., Westcot, D. W.: Water quality for agriculture. FAO Irrigation and Drainage Paper 29, rev. 1. Rome: FAO. (1985)

2. Guan, Z., Lv, J., Bai, P., Guo, X.: Boron removal from aqueous solutions by adsorption - A review. Desalination. 383, 29-37 (2016)

3. Polat, H., Vengosh, A., Pankratov, I., Polat, M.: A new methodology for removal of boron from water by coal and fly ash. Desalination. 164, 173-188 (2004)

4. Yuksel, S., Yurum, Y.: Removal of boron from aqueous solutions by adsorption using fly ash, zeolite, and demineralized lignite. Sep. Sci. Technol. 45, 105-115 (2009)

5. Dionisiou, N., Matsi, T., Misopolinos, N. D.: Use of magnesia for boron removal from irrigation water. J. Environ. Qual. 35, 2222-2228 (2006)

6. Euroslag, & Eurofer: Position paper on the status of ferrous slag. http://projects.gibb.co.za/Portals/3/App%20J13_Position_Paper_April_2012.pdf (2012).

7. Samara, E., Matsi, T., Balidakis, A.: Soil application of sewage sludge stabilized with steelmaking slag and its effect on soil properties and wheat growth. Waste Manag. 68, 378-387 (2017)

8. Goldberg, S.: Reactions of boron with soils. Plant Soil. 193, 35-48 (1997)

9. Duan, J., Su, B.: Removal characteristics of Cd(II) from acidic aqueous solution by modified steel-making slag. Chem. Eng. J. 246, 160-167 (2014)

10. Huifen Y., Wen, M., Weina Z., Zhiyong, W.: Steel slag as multi-functional material for removal of heavy metal ions in wastewater. In: The 2011 International conference on computer distributed control and intelligent environmental monitoring proceedings, pp. 1287-1290. IEEE (2011)

11. Oh, C., Rhee, S., Oh, M., Park, J.: Removal characteristics of As(III) and As(V) from acidic aqueous solution by steel making slag. J. Hazard. Mater. 213-214, 147-155 (2012)

12. Lan, Y. Z., Zhang, S., Wang, J. K., Smith, R. W.: Phosphorus removal using steel slag. Acta Metall. Sin-Engl. 19(6), 449-454 (2006)

13. Mercado-Borrayo, B. M., Schouwenaars, R., González-Chávez, J. L., Ramírez-Zamora, R. M.: Multi-analytical assessment of iron and steel slag characteristics to estimate the removal of metalloids from contaminated water. J. Environ. Sci. Health A. 48(8), 887-895 (2013)

14. Mercado-Borrayo, B. M., Schouwenaars, R., Litter M. I., Ramírez-Zamora, R. M.: Adsorption of boron by metallurgical slag and iron nanoparticles. Adsorpt. Sci. and Technol. 32(2), 117-123. (2014)

15. Keren, R.: Boron. In: D. L. Sparks (Ed.), Methods of soil analysis - Part 3 - Chemical methods, SSSA Book Series 5, pp. 603-626. Madison, WI: SSSA and ASA (1996)

16. Polowczyk, I., Ulatowska, J., Kozlecki, T., Bastrzyk, A., Sawinski, W.: Studies on removal of boron from aqueous solution by fly ash agglomerates. Desalination. 310, 93-101. (2013)

17. Goldberg, S., Forster, H. S.: Boron sorption on calcareous soils and reference calcites. Soil Sci. 152(4), 304-310 (1991)

18. Goldberg, S., & R.A. Glaubig, R. A.: Boron adsorption on aluminium and iron oxides. Soil Sci. Soc. Am. J. 49, 1374-1379 (1985)

Figure captions

Fig. 1 Experimental data of B adsorption on the steelmaking slag and the fitted non-linear Langmuir and Freundlich isotherms

Fig. 2 X-ray diffraction patterns of steelmaking slag, before and after equilibration with H_2O and drying

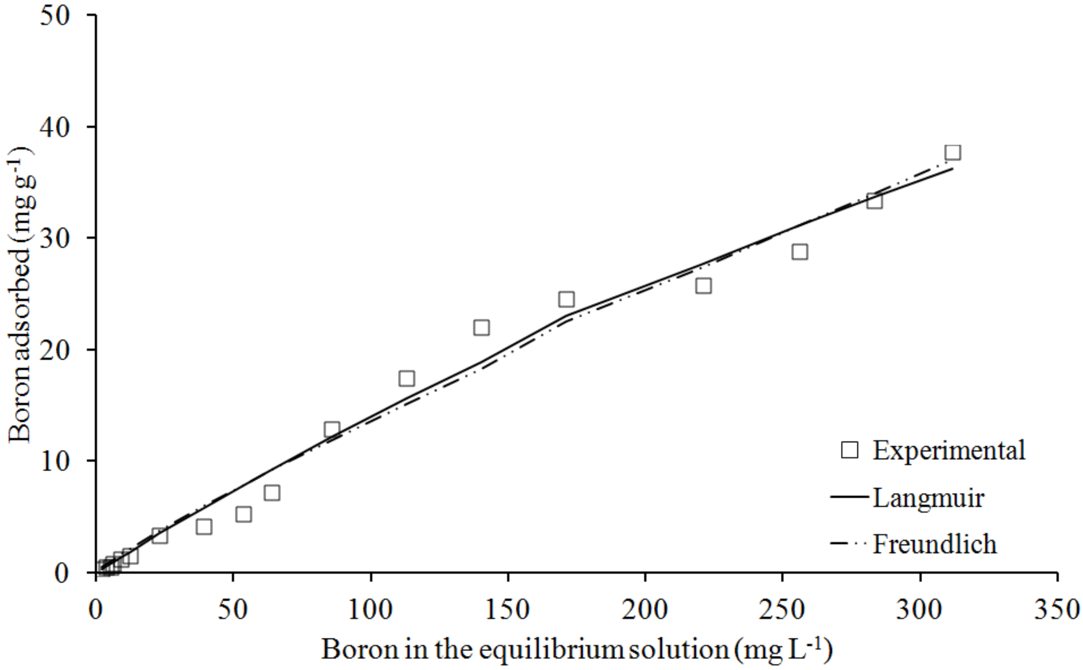
Table 1 The parameters of the nonlinear Langmuir and Freundlich equations and their respective *F*-test values, for B adsorption on the steelmaking slag

Equation	Parameters		*F*-test
Langmuir	M (mg g^{-1})	K (L mg^{-1})	1107***
	145[†] ± 47[‡]	0.001±0.0004	
Freundlich	k (mg kg^{-1})	n	953***
	236 ± 66	0.88 ± 0.05	

[†] Mean

[‡] Standard deviation

*** $p \leq 0.001$



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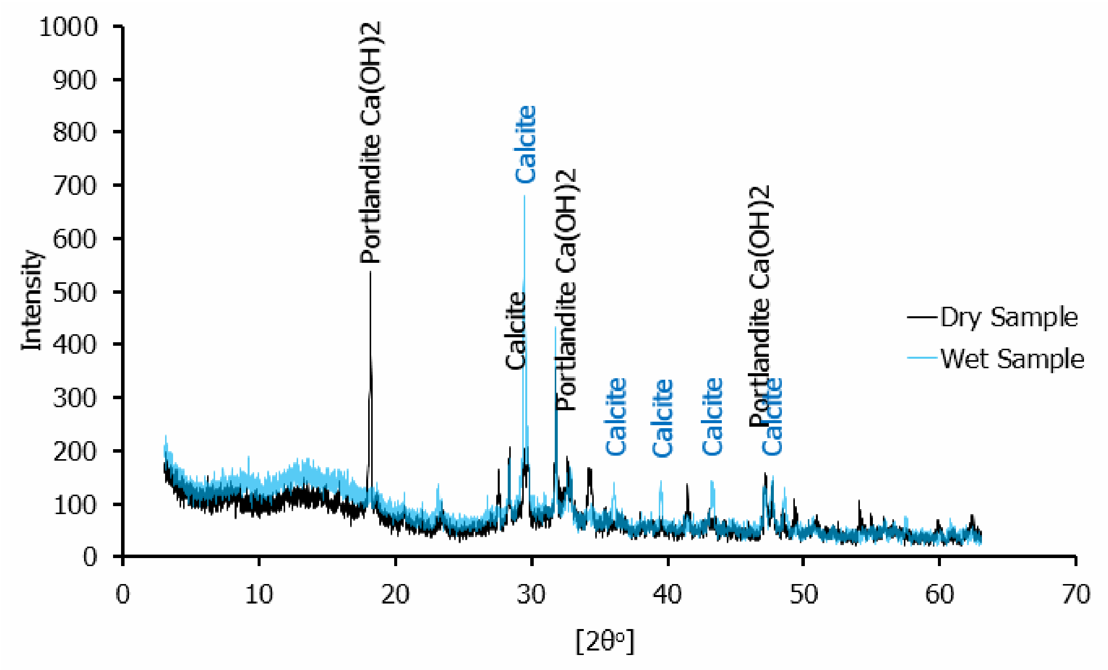

Fig. 2 X-ray diffraction patterns of steelmaking slag, before and after equilibration with H_2O and drying