Adsorption of Boron by Metallurgical Slag and Iron Nanoparticles

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Reprinted from

Adsorption Science & Technology

2014 Volume 32 Number 2&3

Multi-Science Publishing Co. Ltd.
5 Wates Way, Brentwood, Essex CM15 9TB, United Kingdom

Adsorption of Boron by Metallurgical Slag and Iron Nanoparticles

B.M. Mercado-Borrayo[1], R. Schouwenaars[2], M.I. Litter[3] and R.M. Ramirez-Zamora[1,*] *(1) Instituto de Ingeniería, Coordinación de Ingeniería Ambiental, Universidad Nacional Autónoma de México (UNAM), Coyoacán 04510, DF, Mexico. (2) Facultad de Ingeniería, Departamento de Materiales y Manufactura, DIMEI, Universidad Nacional Autónoma de México, Coyoacán 04510, DF, Mexico. (3) Comisión Nacional de Energía Atómica, San Martín, Provincia de Buenos Aires, 1650, Argentina.*

(Received date: 16 September 2013; Accepted date: 15 February 2014)

ABSTRACT: Boron is a problematic pollutant because of the difficulty involved in removing it from water with an acceptable cost-to-benefit ratio, especially at extremely high concentrations (600 mg B/l). It is also necessary to remove the pollutant to comply with the quality criteria for drinking water (1 mg B/l) and even for agricultural irrigation purposes (0.5–15 mg B/l depending on crop tolerance). Although some newly proposed water-treatment technologies use economical adsorbents, they are unable to achieve the residual concentrations. The aim of this work is to show that adsorption using metallurgical slags (SL) can be used either as a pre-treatment of the zero-valent iron nanoparticles (nano-Fe^0) or as a final treatment itself for removing boron at high concentrations to obtain effluents complying with the standards established for drinking water and wastewater reuse. Adsorption tests (kinetics and isotherms) were carried out for both adsorbents. The slags showed good results as an adsorbent for boron removal in the pre-treatment and final treatment stages, with a very low cost compared with nano-Fe^0. The use of slags instead of expensive commercial adsorbents makes adsorption of water with high boron concentrations feasible, and allows obtaining treated wastewater for agricultural irrigation of very tolerant crops.

1. INTRODUCTION

Boron (B) is a semimetal found in water as boric acid (H_3BO_3) and tetraborate $[B(OH)_4]^-$ (Kabay *et al*. 2007). This metalloid causes teratogenic damage in different types of living beings (Moss and Nagpal 2003), but none of the identified research in this field concludes that this pollutant actually produces this effect in humans (Robbins *et al*. 2010). However, the guidelines recommended by the World Health Organization for drinking water establish a maximum permissible concentration of 1 mg B/l (USEPA 1994), and international standards for the concentration limit of boron in treated wastewater for irrigation recommend a range from 0.5 to 15 mg/l. These values were established based on the tolerance of various crops (Moss and Nagpal 2003; Table 1).

Several water-treatment technologies are reported for the removal of boron, including membrane processes (Hilal *et al*. 2011), electrocoagulation (Sayiner *et al*. 2008), coagulation–flocculation (Yilmaz *et al*. 2007), ion exchange (Li *et al*. 2011) and adsorption using commercial materials such as hydrotalcite (Yoshioka *et al*. 2007), amberlite IRA 743 (Boncukcuoglu *et al*. 2004) and *N*-methyl glucamine (Kabay *et al*. 2007); however, these adsorbents are expensive and none of them have been able to remove this pollutant from water at high initial concentrations (600 mg/l reported for some underground sources; Kabay *et al*. 2009) to standard values recommended in drinking water.

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*Author to whom all correspondence should be addressed. E-mail: rmrz@pumas.iingen.unam.mx; RRamirezZ@iingen.unam.mx (R.M. Ramírez-Zamora).

TABLE 1. Sensitivity of Different Crops to Boron (Moss and Nagpal 2003)

Tolerance	mg B/l	Examples of crops
Very sensitive	<0.5	Blackberry and lemon
Sensitive	0.5–0.75	Cherry, plum, grapes, beans, onion, garlic, sweet potato, wheat, barley, sunflower, strawberry, artichoke, avocado, grapefruit, orange, persimmon, apricot, grape, walnut, sweet potato, sesame and peanut
Moderately sensitive	1–2	Red pepper, peas, carrot, radish, potato, cucumber, broccoli and lettuce
Moderately tolerant	2–4	Cabbage, turnips, barley, oats, corn, snuff, mustard, eggplant, melon and cauliflower
Tolerant	4–6	Sorghum, tomato, alfalfa, parsley and cabbage
Very tolerant	6–15	Asparagus, sweet corn, cotton and celery

For the exposed economic reasons, non-conventional adsorbents have been studied instead of commercial adsorbents to minimize costs, cover small-scale processes, while considering the social acceptance and waste treatment (Litter *et al.* 2010). The most efficient economic adsorbents of boron are fly ash (8 hours, 1–5 g of fly ash/l, pH = 2–11, $[600 \text{ mg B/l}]_0$, 90% for the highest removal efficiency) (Öztürk and Kavak 2005) and red mud (4 hours, 1–8 g of red mud/l, pH = 2–7, $[12–200 \text{ mg B/l}]_0$, 95% for the highest removal efficiency) (Cengeloglu *et al.* 2007). However, as mentioned in the cited reports, these optional adsorbents have not been able to remove this pollutant from high concentrations to drinking-water levels. Another solution could be the combination of economic (as pre-treatment) and commercial (for polishing purposes) adsorbents. Metallurgical slag, an industrial by-product generated worldwide on large scales, is economical and has been proven to be one of the most efficient adsorbents for removing several types of heavy metals, because these materials have several compounds in their structure that can adsorb these pollutants. This pre-treatment can be combined with the oxide-reduction/adsorption process of zero-valent iron nanoparticles (nano-Fe^0), which is an emerging technology because these nanoadsorbents have a comparatively high specific surface area and form highly efficient compounds of iron [Fe-α, magnetite (Fe_3O_4), iron oxide (FeO)]. However, no reports have been identified to evaluate the adsorption capacity of nano-Fe^0 for the removal of boron.

In this paper, we assess the feasibility of the boron adsorption process, using metallurgical slag in a two-step adsorption method with zero-valent iron nanoparticles, for the removal of this pollutant from very high concentrations to guidelines proposed for the irrigation of sensitive crops and levels established for drinking-water standards.

2. MATERIALS AND METHODS

2.1. Materials

The following were used in our experiments: steel slag generated by the basic oxygen furnace method containing 38 wt% $Mg(OH)_2$, with 7.3 m^2/g surface area and pH_{pzc} 8.5. In addition, zero-valent iron nanoparticles containing iron (Fe^0), maghemite (Fe_2O_3) and magnetite (Fe_3O_4) along with minor amounts of more amorphous phases with an average surface area of 60 m^2/g were also used. The complete physicochemical characteristics of the slag and zero-valent iron nanoparticles have been reported previously (Morgada *et al.* 2009; Mercado-Borrayo *et al.* 2013). The boron compound used to prepare the working solutions was boric acid (99.9%; Bruker).

2.2. Systems and Experimental Techniques

2.2.1. Adsorption kinetics

A 600 mg B/l solution prepared in distilled water was mixed with 7 g/l of slag. This suspension was placed for oscillatory mixing on a shaker at 250 rpm (Barnstead/Lab-line) and at a constant temperature of 25°C. At time intervals of 30, 60, 90, 240 and 360 minutes, 1-ml samples were collected and filtered on a 0.45-μm membrane (HAWP cellulose esters; Millipore). The filtrate was analyzed to determine the residual concentration of boron by the spectrophotometric carmine method (Spielhotz *et al.* 1973). For the trials using nano-Fe^0, the lowest boron concentration obtained using the slag was chosen to prepare a boron solution to be treated using these materials. The adsorbent dose was 1.5 g/l, which was established in previous studies; the amount of iron in the nano-Fe^0 dose was also chosen as established in previous studies. The same protocol used for the kinetic tests using slag was also carried out for nano-Fe^0. All kinetics tests were repeated five times for determining the equilibrium adsorption time.

2.2.1.1. Adsorption isotherms

The adsorption isotherm tests were performed in batch reactors using the bottle-point method. Solutions of 600 mg B/l for slags and 15 mg B/l for zero-valent iron nanoparticles were prepared in distilled water. Each solution (100 ml) was added separately in six 200-ml reactors. Different doses of slag (0, 0.5, 1, 3, 7 and 9 g/l) and zero-valent iron nanoparticles (0, 1, 1.5, 2, 2.5 and 3 g/l) were added; the suspensions were placed for oscillatory mixing on a shaker. Upon reaching the equilibrium time, the mixtures were filtered and analyzed to quantify residual boron. The isotherm tests were performed five times.

2.3. Analytical Techniques

The quantification of boron was performed using the spectrophotometric carmine method (Spielhotz *et al.* 1973), where in the presence of H_2SO_4 (J.T. Baker, 97.7%) boron is found in the cationic form B^{3+} (Figure 1). This species produces a cationic complex with the carmine indicator causing a colour change in the solution. The detection limit of this method is 0.2 mg B/l and the calibration curve showed a linear correlation coefficient r = 0.9997.

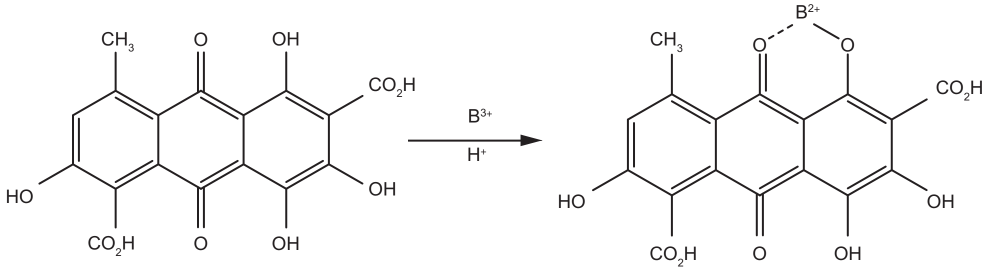

Figure 1. Carmine reaction method for the quantification of boron.

3. RESULTS

3.1. Adsorption Kinetics

We evaluated three adsorption kinetic models, namely, pseudo first order, pseudo second order and Elovich (Hameed *et al*. 2008; Table 2) using data of both adsorbents; the results from each of the adsorption kinetics were statistically analyzed by calculating the variance and standard deviation. Based on these two statistical parameters, the variations of each equilibrium capacity were calculated.

The pseudo-second-order model showed the best fit to the data (Figure 2); this model was developed for the chemisorption processes. This agrees well with the reported adsorption mechanism of semimetals to crystalline phases of Fe-α and $Mg(OH)_2$, which are present in the zero-valent iron nanoparticles and slag, respectively. The adsorbate–adsorbent interactions involve covalent bonding (chemisorption). The bond is produced between the positively hydroxylated iron and magnesium species present on the slag surface as shown in Figure 3, in which Me = iron or magnesium, as established for another similar metalloid such as arsenic (Biterna *et al*. 2007; García-Soto *et al*. 2009).

TABLE 2. Adsorption Kinetics Models

Model	Equation	Symbols used
Pseudo first order	$d_q/d_t = k_1(q_e - q)$	q_e = equilibrium adsorption capacity (mg/g) q = adsorption capacity at time t (mg/g) t = time (minute) k_1 = pseudo-first-order rate constant (l/minute)
Pseudo second order	$d_q/d_t = k_2(q_e - q)^2$	qe = the equilibrium adsorption capacity (mg/g) q_t = adsorption capacity at time t (mg/g) t = time (minute) k_2 = pseudo-second-order rate constant (g/mg minute)
Elovich	$d_q/d_t = \alpha \exp(-\beta q_t)$	q_t = adsorption capacity at time t (mg/g) t = time (minute) α = initial adsorption speed (mg/g minute) β = constant (g/mg)

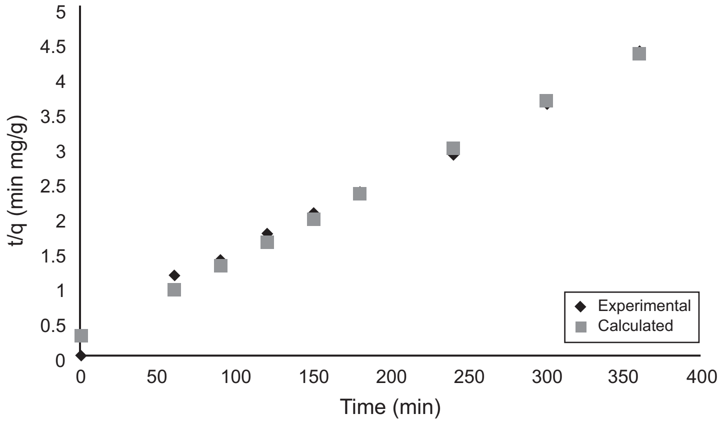

Figure 2. Pseudo-second-order kinetic modelling for boron removal by slag.

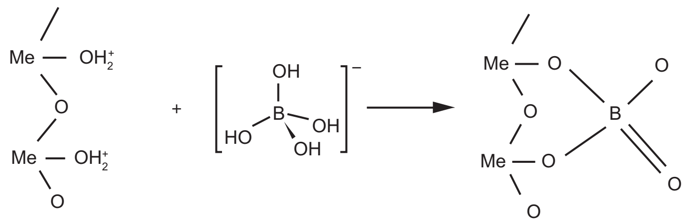

Figure 3. Mechanism of boron removal on the slag surface.

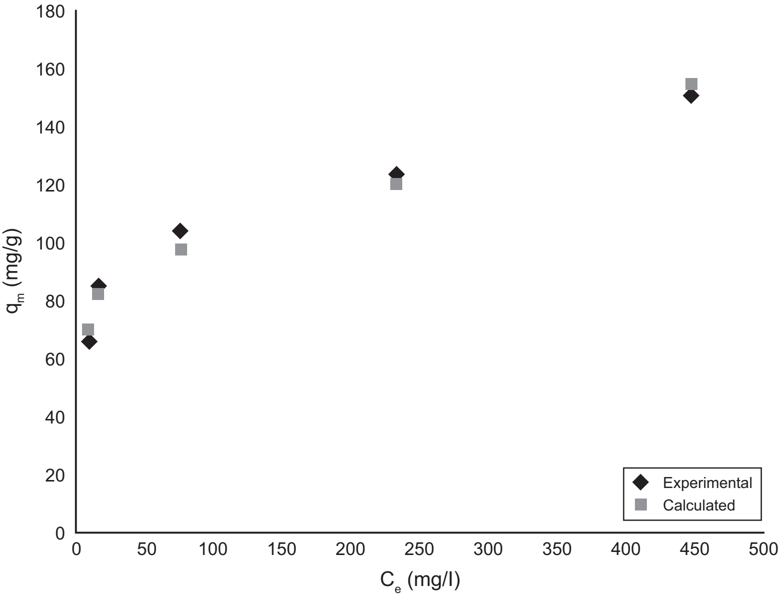

Figure 4. Koble-Corrigan isotherm of boron removed by slag.

3.2. Adsorption Isotherms

The following 12 adsorption isotherm models were evaluated: Brunauer–Emmett–Teller, Dubinin–Radushkevich, Freundlich, Khan, Sips, Koble–Corrigan, Langmuir, Langmuir–Freundlich, MacMillan–Teller, Redlich–Peterson, Temkin and Toth to select the one that describes the experimental data more adequately (Foo and Hameed 2010).

The fitting constants in the adsorption models were calculated for all 12 using numerical procedures. The error was calculated based on the nonlinear Chi-square test. The model that best fits the boron adsorption data was the Koble–Corrigan model for both adsorbents. This model was developed for heterogeneous systems with high initial concentrations of adsorbate, as is the case in this work [>600 mg B/l] (Figure 4).

The Koble–Corrigan model (three-parameter empirical equation) is

$$q_m = \frac{K_T C_e^n}{(a_T + C_e)^n} \tag{1}$$

where K_T ($l^n mg^{1-n}/g$), a_t [$(l/mg)^n$] and n are the Koble-Corrigan's parameters.

TABLE 3. Best Experimental Results Obtained for Boron Removal Using Slag and Nano-Fe^0 and Adsorbent Costs

Adsorbent	Experimental conditions	$[B]_{fin}$ (mg/l) (Removal efficiency)	Model and parameters of adsorption isotherms (n = 30)	Model and parameters of adsorption kinetics (n = 30)	USD/kg
Slags	4 hours, 7 g slag/l, pH = 11, $[600 \text{ mg B/l}]_0$	15 (99.73%)	Koble–Corrigan $q_m = 1.75$ mg/g A = 199.70 B = 0.28 n = 0.11 $\chi^2 = 4.28$	Pseudo second order $T_{eq} = 4$ hours $k_2 = 0.98$ mg/g minute r = 0.9973 $\sigma^2 = 18.14$ $\sigma = 4.26$	0.025
nano-Fe^0	2 hours, 1.5 g nano-Fe^0/l, pH = 8, $[15 \text{ g B/l}]_0$	1 (93.33%)	Koble–Corrigan $q_m = 4.51$ mg/g A = 595.42 B = 0.01 n = 0.96 $\chi^2 = 2.22$	Pseudo second order $T_{eq} = 3$ hours $k_2 = 0.26$ mg/g minute r = 0.9973 $\sigma^2 = 15.13$ $\sigma = 3.89$	122

TABLE 4. pH and Zeta-Potential Conditions for the Best Adsorption Efficiency of Boron

Material	pH	Zeta potential value (mv)
Slag	11	+20
Zero-valent iron nanoparticles	8	+10

The best boron adsorption results, the main parameters calculated for the best-fit kinetic and isotherm models and the materials costs are shown in Table 3. The boron-removal efficiencies for both adsorbents were higher than 90%, producing effluents with residual concentrations complying with the irrigation guidelines using slags and the drinking-water standards using zero-valent iron nanoparticles. The boron-removal efficiency for slag (99.73%) was significantly higher than values reported for fly ash (90%) and red mud (90%), at similar conditions, especially for fly ash. At the basic pH values used in the boron-removal experiments of this work, the average surface charge values were positive for slag and zero-valent iron nanoparticles (Table 4), and according to the predominance species diagram, the only boron-charged specie found at these conditions is $B(OH)_4$-; thus, it is expected that the adsorption process of this metalloid will be favoured in both cases.

The adsorption process with slag showed to be a good pre-treatment step because it produced an effluent with a boron concentration (15 mg/l) low enough to be reduced subsequently by nano-Fe^0 to drinking-water standard levels.

The residual boron concentration obtained for each adsorbent (Table 1) is within the limits of international standards proposed for drinking water and for irrigation of moderately sensitive crops and for very tolerant crops, using nano-Fe^0 and slags, respectively. The slag showed a higher removal efficiency than nano-Fe^0 (99.73% vs. 93.33%), but the qm of nano-Fe^0 was almost two times as high as the value of SL, and the time for reaching equilibrium was also 50% lower than the slag value. This can be attributed to the specific surface area of nano-Fe^0, which is approximately three times higher than that of slag.

By contrast, for determining the slag feasibility to be used in the boron adsorption process, it is important to consider the material, which is 4300 times more economical than nano-Fe^0.

4. CONCLUSIONS

It was shown that metallurgical slag can have a high feasibility for boron removal, and thus can be used as an adsorbent for the removal of this pollutant from very high concentrations to guidelines established for the irrigation of sensitive crops, and to levels established for drinking-water standards.

Slag can be used either in the main treatment for removing boron or in the pre-treatment step of the adsorption process along with nano-Fe^0, because this material was able to reduce by itself very high concentrations of boron to levels recommended in guidelines for the irrigation of very tolerant crops or along with nano-Fe^0 for producing an effluent with boron concentrations complying with the drinking-water standards. In addition, the water-treatment cost with slag can be significantly lower than the value calculated for nano-Fe^0.

REFERENCES

Biterna, M., Ardistsoglou, A., Tsikouras, E. and Vousta, D. (2007) *J. Hazard. Mater.*, **149**, 548.

Boncukcuoglu, R., Yilmaz, A.E., Kocakerim, M.M. and Copur, M. (2004) *Desalination*. **160**, 159.

Cengeloglu, Y., Tor, A., Arslan, G., Ersoz, M. and Gezgin, S. (2007) *J. Hazard. Mater.* **21**, 415.

Foo, K.Y. and Hameed, B.H. (2010) *Chem. Eng. J.*, **165**, 2.

García-Soto, M.M. and Muñoz, C. (2009) *Desalination*. **249**, 626.

Hameed, B.H., Chin, L.H. and Rengaraj, S. (2008) *Desalination*. **225**, 185.

Hilal, N., Kim, G.J. and Simerfield, C. (2011) *Desalination*. **273**, 23.

Kabay, N., Sarp, S., Yüksel, M., Arar, Ö. and Bryjak, M. (2007) *React. Funct. Polym.*, **67**, 1643.

Kabay, N., Yilmaz-Ipek, I., Soroko, I., Makowski, M., Kirmizisakal, O., Yag, S., Bryjak, M. and Yuksel, M. (2009) *Desalination*. **241**, 167.

Li, X., Liu, R., Wu, S., Liu, J., Cai, S. and Chen, D. (2011) *J. Colloid Interface Sci*. **361**, 232.

Litter, M.I., Morgada, M.E. and Bundschuh, J. (2010) *Environ. Pollut*. **158**, 1105.

Mercado-Borrayo, B.M., Schouwenaars, R., González-Chávez, J.L. and Ramírez-Zamora, R.M. (2013) *J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng.*, **48**, 887.

Morgada, M.E., Levy, I.K., Salomone, V., Farías, S.S., López, G. and Litter, M.I. (2009) *Catal. Today*. **143**, 261.

Moss, S.A. and Nagpal, N.P. (2003) *Ambient Water Quality Guidelines for Boron*, Ministry of Environment, Government of Canada, British Columbia, Canada, pp. 1–113.

Öztürk, N. and Kavak, D. (2005) *J. Hazard. Mater.* **127**, 81.

Robbins, W.A., Xun, L., Jia, J., Kennedy, N., Elashoff, D.A. and Ping, L. (2010) *Reprod. Toxicol*. **29**, 184.

Sayiner, G., Kandemirli, F. and Dimoglo, A. (2008) *Desalination*. **230**, 205.

Spielholtz, G.I., Toralballa, G.C. and Willsen, J.J. (1973) *Mikrochim. Acta*. **62**, 649.

USEPA (1994) *Guidelines for Water Reuse*, Washington, DC.

Yilmaz, E., Boncukcuoglu, R. and Kocakerim, M. (2007) *J. Hazard. Mater.* **149**, 475.

Yoshioka, T., Kameda, Y., Myhara, M., Uchida, M., Mixoguchi, T. and Okuwaki, A. (2007) *Chemosphere*. **69**, 823.