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An analysis of boron removal from water using modified zero-valent iron nanoparticles

Hassan Khorsandi[a], Aliye Azarnioush[b,*], Ali-Ahmad Aghapour[a], Sepideh Nemati[b], Sima Karimzadeh[b], Hamid-Reza Khalkhali[c]

[a]*Social Determinants of Health Research Center and Environmental Health Engineering Department, School of Public Health, Urmia Medical Sciences University, Urmia, Iran, emails: hassankhorsandi@yahoo.com (H. Khorsandi), aaaghapour@gmail.com (A.A. Aghapour)*

[b]*Environmental Health Engineering Department, School of Public Health, Urmia Medical Sciences University, Urmia, Iran, Tel. +98 44 32752300; Fax: +98 44 32770047; emails: aliye.azarnoosh@yahoo.com (A. Azarnioush), nemati.sepid@gmail.com (S. Nemati), sima.karimzade@yahoo.com (S. Karimzadeh)*

[c]*Biostatistics and Epidemiology Department, School of Medicine, Urmia Medical Sciences University, Urmia, Iran, email: khalkhali@umsu.ac.ir (H.R. Khalkhali)*

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ABSTRACT

Considering the necessity of boron removal from water and its unexpected resistance against a majority of common processes, the use of efficient procedures for its removal seems more necessary than ever. Therefore, the aim of the present study is to analyze boron removal from water using zero-valent iron nanoparticles (nZVI) stabilized by two biopolymers. Modified nZVI was synthesized using the method of ferrous sulfate reduction. Structural features, chemical mixture, and morphological characteristics of selected nanoparticles (starch-nZVI [S-nZVI]) were confirmed by X-ray diffraction and scanning electron microscope. The function of S-nZVI in boron removal was examined under the influence of various factors including initial concentration of boron, S-nZVI dose, pH, and contact time in batch conditions. Boron was measured by the standard carmine method. The results showed that 1 mg/L of S-nZVI can reduce up to 20 mg/L of boron to less than its maximum allowable concentration in the pH of 8.5 and reaction time of 90 min. Kinetics of boron adsorption by S-nZVI follows pseudo-second-order ($R^2 = 0.999$) upon which adsorption capacity of boron by S-nZVI at equilibrium time fluctuates between 4.55 mg/g at initial concentration of 5 mg/L and 48.78 mg/g at initial concentration of 50 mg/L. Furthermore, boron adsorption by S-nZVI is more compatible with Langmuir isotherm ($R^2 = 0.93$). Accordingly, the maximum adsorption capacity of boron by S-nZVI was determined as 128.2 mg/g. Hence, as an appropriate, eco-friendly reactant, nZVI modified by starch can be used in boron removal from aquatic environments.

Keywords: Boron; Carboxymethyl cellulose; Starch; Water; Zero-valent iron nanoparticles

1. Introduction

Boron is a metalloid ubiquitous element in rock, soil, and water in various forms of boric acid and borates, which is never found in nature as elemental form [1,2].

Considering their extensive use in various industries including glasswork, ceramics, porcelain, leather, semiconductors, papermaking, pharmaceuticals and cosmetics, corrosion inhibitors in antifreezes, carpets, agricultural fertilizers, pesticides, insecticides, herbicides, detergents, hand cleansings, disinfectants, food preservatives, and flame retardants; boron compounds are known as one of the factors

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* Corresponding author.

threatening the quality of water resources [3,4]. Boron is an essential element for humans and animals so that it is necessary for fetal growth, bone metabolism and adsorption of nutrients, but its excessive amounts effect a change in blood composition and cause a disorder of cardiovascular, nervous, and reproductive systems [1,5,6].

Boron is a vital micronutrient for plants and plays a prominent role in cell wall formation, metabolism of carbohydrate, nucleic acid synthesis, enzymatic reactions, and membrane transportation. If, however, its contraction exceeds the required limit, boron, due to its production of toxic effects, brings about photosynthesis inhibition, deposition of chlorophyll, yellowish spots on the leaves, poor budding, dwarfing, and finally the death of plants [2,5,6].

In 2011, WHO proposed 2.4 mg/L of boron as the allowed maximum of boron concentration in drinking water on the basis of human health considerations [4]. The recommended amount of boron in drinking water in the European Union is 1.0 mg/L [6]. This is while the average concentration of boron is 30 mg/kg in soil, 4.5 mg/L in seawater, and 0.3–100 mg/L in groundwater [1,2].

Considering the negative effects of boron on humans and agricultural products, the study of effective ways on removal of its compounds from water is necessary. Such processes as coagulation–flocculation [7], adsorption by commercial materials [8], reverse osmosis [9], ion-exchange boron selective resins [10], thermal and electrochemical methods [11] have already been studied in boron removal, all of which have often some limitations including high cost, high energy consumption, and low efficiency [5].

In recent years, the use of zero-valent metals including Fe^0, Zn^0, Sn^0, and Al^0 for the removal of various pollutants from water have been frequently studied, among which the use of zero-valent iron nanoparticles (nZVI), as an efficient and environment-friendly sorbent and reluctant, is more popular due to their higher surface area and shape dependent properties for removing various organic pollutants including chlorinated methane, organochlorine pesticides, chlorinated phenols, organic dyes, and most heavy metals such as Ag^{2+}, As(III), Ba^{2+}, Cd^{2+}, Co^{2+}, Cr(VI), Cu^{2+}, Ni^{2+}, and Pb^{2+} [12–14].

Notwithstanding advantages, nZVI quickly accumulate in aquatic environment and consequently their efficiency in pollutant removal decreases [15,16]. Today, many different ways including admixtures of other metals to nZVI, coating the surface of nZVI, emulsification of nZVI, and deposition of nZVI on a carrier are used so as to modify nZVI particles and increase their stability and efficiency [15].

Various immobilization technologies are being developed for nZVI stabilization, such as starch, carboxymethyl cellulose (CMC), guar gum, kaolin, and Ethylenediaminetetraacetic acid (EDTA), all of which decrease aggregation and improve dispersion as well as stabilization [15–18].

Among various stabilizers, more attention has been paid to green polysaccharides, especially starch and CMC for prevention of accumulation of nZVI and an increase in their reactivity [15].

Considering the necessity of boron removal from water and its unexpected resistance against many common processes, the use of modern, efficient, and easy procedures for its removal seems more necessary than ever. Therefore, the aim of the present study is to analyze boron removal from water using nZVI stabilized by starch (S-nZVI) and CMC (CMC-nZVI) biopolymers in the first time. According to our reviews, there are no sufficient comprehensive results available in this area.

2. Methods

2.1. Synthesis of nanoparticles

In this study, nZVI were synthesized using ferrous *sulfate* reduction method [19]. In this method, first, 0.14 mM solution of ferrous sulfate ($FeSO_4.7H_2O$) with 0.2 wt% of starch or CMC as a stabilizer was poured in a three-necked flask and stirred for a few minutes so as to form iron complexion and stabilizer. Then, 0.5 mM solution of sodium borohydride ($NaBH_4$) was added drop by drop and under intense mixing in the presence of nitrogen to the contents of flask. In this case, ferrous sulfate is reduced to zero-valent iron by sodium borohydride. After the addition of all borohydride and in order to complete the reaction, the resulting mixture was stirred for 15 min so as to make the H_2 exit the flask. After the reaction, black iron nanoparticles were produced and after the separation by centrifuge were washed away three times with ethanol (96%) at a speed of 4,000 rpm within 5 min for deionization and dried up in vacuum desiccator at the laboratory temperature for 24 h. It is worth noting that in order to prevent the oxidation of nZVI, all the processes of nanoparticles synthesis were conducted under vacuum conditions and since a byproduct of the reactions related to the synthesis of nZVI is hydrogen, all the processes of synthesis were conducted under a fume hood.

Non-stabilized nanoparticles were also synthesized in a similar way but in the absence of a stabilizer and their efficiency in boron removal under the same conditions was compared with stabilized nanoparticles. All the materials used were Merck products.

Nanoparticles map and their size were analyzed and confirmed by scanning electron microscope (SEM; VEGA\\TESCAN, Czech Republic). Composite materials were identified using X-ray diffraction (XRD; Explorer, G.N.R., Italy) whereas chemical elements and their concentration in mixture of stabilized nanoparticles were characterized by energy dispersive analysis X-ray (EDAX; VEGA\\TESCAN, Czech Republic).

2.2. Experiments for boron removal by nZVI in batch conditions

In this study, nZVI were synthesized and used daily. A stock solution of boron was produced by dissolving boric acid (H_3BO_3) in distilled water, by the use of which synthetic solutions with specific concentrations were created for conducting experiments. Boron removal by iron nanoparticles in a 250-mL batch reactor with complete mixing (at 150 rpm) was examined under laboratory conditions. After comparing efficiency of nZVI, S-nZVI, and CMC-nZVI and choosing suitable nanoparticles, we studied the effect of reaction time (5, 15, 30, 60, 90, and 120 min), pH (5, 8.5, and 11), the concentration of iron nanoparticles (0.2, 0.5, 1, and 2 g/L), and initial concentration of boron (5, 10, 20, and 50 mg/L) on boron removal. At the end of each process, 5 min were allotted to sedimentation of nanoparticles. Then, its supernatant was centrifuged at 3,000 rpm for 5 min and was filtered through 0.22 μm syringe filters. The concentration of remaining boron was determined according to standard methods for the examination of water and wastewater and on the basis of carmine colorimetric method [20] at the wavelength of 605 nm by DR5000 spectrophotometer (Hach, Germany). We used the measurement of standard samples and the repetition of all processes of experiments in order to prove the validity and the reliability of results.

3. Results and discussion

3.1. *The effect of stabilization of nZVI on boron removal*

In this study, in order to prevent the electrostatic adsorption between nanoparticles and their accumulation, the coating of nZVI particles were conducted separately using starch and CMC biopolymers for their availability, low cost, and eco-friendly features.

The results of comparing the efficiency of boron removal by S-nZVI, CMC-nZVI, and non-stabilized nZVI are presented in Fig. 1. According to the figure, S-nZVI has higher efficiency in boron removal compared with the other two forms of iron nanoparticles, and therefore, this type of nZVI was selected to analyze boron removal.

As indicated by Fig. 1, the efficiency of S-nZVI in removing 10 mg/L of boron at equilibrium time of 30 min was approximately 6% more than nZVI, so that providing 1 mg/L of boron as the maximum allowable concentration in drinking water [1] through S-nZVI was obtained approximately 1 h quicker than the reaction with nZVI.

3.2. *Features of synthesized and modified nZVI*

Fig. 2 shows an SEM image of nZVI modified by starch. As indicated, nanoparticles are spherical and their size is <100 nm. Fig. 3 illustrates XRD analysis of modified nZVI. At angles of 44.48°, 65°, 82.1°, and 99°, the curve has the highest peak that according to the standard of ICDD Card# 06-0696 [21,22], it indicates the presence of nZVI. Fig. 4 shows an EDAX picture of synthesized nanoparticles which indicates a purity of 86.36% of zero-valent iron in these nanoparticles.

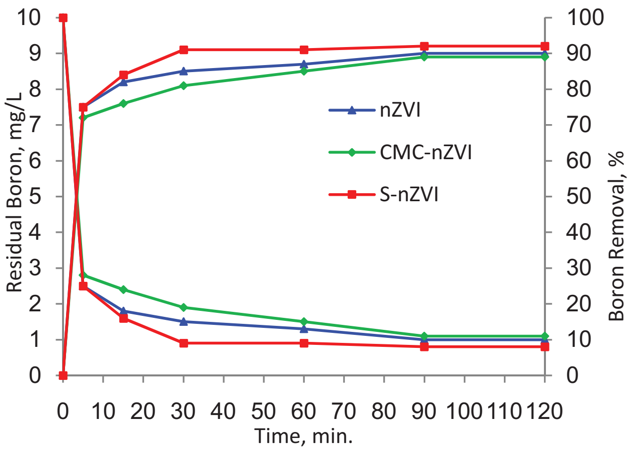


Fig. 1. A comparison of efficiency of boron removal by a variety of nZVI (initial boron = 10 mg/L, nZVI dose = 1 g/L, pH = 8.5).

3.3. *Effect of process conditions on boron removal by S-NZVI*

3.3.1. *Effect of pH*

The results of the effect of pH on boron removal are illustrated in Fig. 5. Since at acidic pH, due to the dissolution of nanoparticles and an increase in viscosity, the efficiency of S-nZVI decreases, the efficiency of boron removal at pH of 5 has the lowest amount. This finding is consistent with the results of An et al. [23] in arsenic removal using magnetite nanoparticles coated with starch at the pH of 3.2.

The highest efficiency of born removal was achieved at pH of 8.5, but as pH increases to 11, the removal efficiency decreases again. At pH values of >10, on the one hand boron

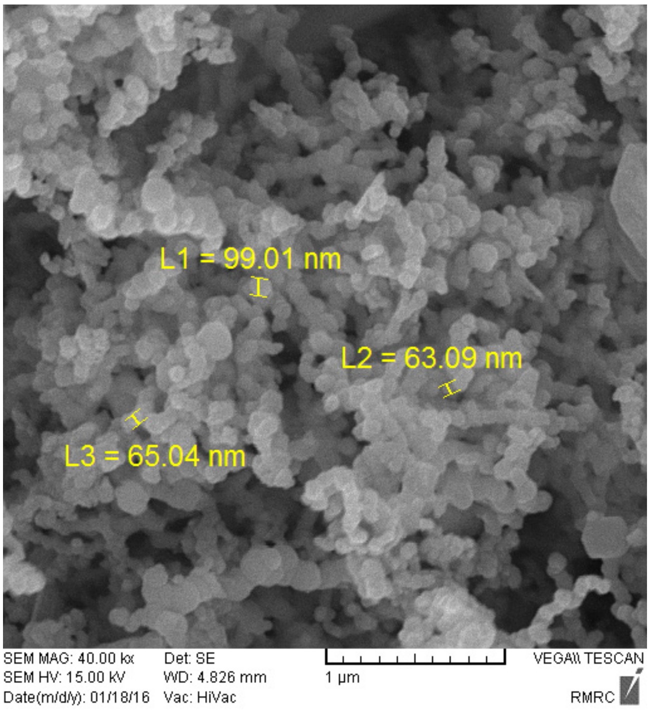


Fig. 2. An SEM image of zero-valent iron nanoparticles modified by starch.

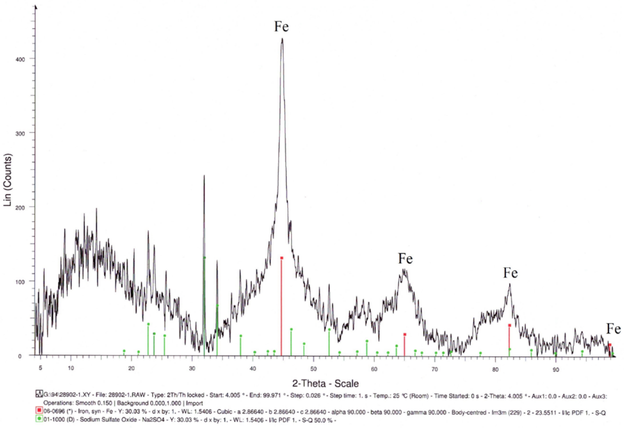


Fig. 3. An XRD pattern of zero-valent iron nanoparticles modified by starch.

converts to $B(OH)_4^-$, but on the other hand surface adsorbent is negatively charged because of OH^- ions adsorption. As a consequence, due to the repulsive force between the adsorbent and negatively charged boron molecules, the removal efficiency decreases [24]. Therefore, the highest efficiency of boron removal in this study was achieved at the pH of 8.5. Accordingly, this pH was considered as optimum pH for boron removal.

3.3.2. The effect of initial concentration of boron

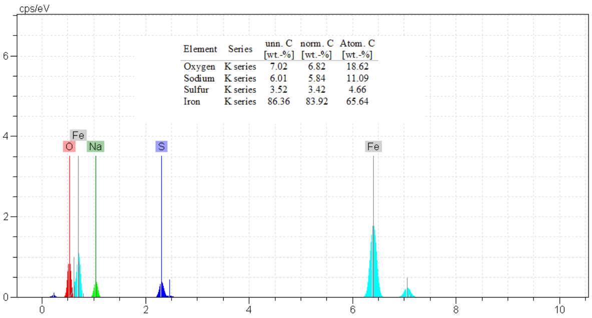
According to the results illustrated in Fig. 6, with increasing initial concentration of boron, adsorption capacity and the efficiency of boron removal by S-nZVI increases. However, reaction time for achieving the acceptable remaining concentration increases too.

Based on the results, the turning point of changes in adsorption capacity and the remaining concentration in most initial concentrations of boron confirm 30 min as equilibrium time. Nevertheless, providing the maximum acceptable concentration of boron at equilibrium time of 30 min in all studied concentrations was not feasible.

Although the limited number of available sites at a dose of adsorbent has inhibitory effect on adsorption effeiciency by increasing the concentration of pollutants [25–28], in the present study, due to the reduction in resistance to adsorption and transfer of boron from water to S-nZVI, with an increase in the initial concentration of boron, the removal efficiency and boron adsorption capacity, as shown in Fig. 6, increase too. Thus, nZVI can remove the concentrations of <20 mg/L of boron within 90 min at an optimal level.

3.3.3. The effect of S-nZVI concentration

The results of the effect of different amounts of nanoparticles on boron removal efficiency are shown in Fig. 7. These results indicate that by an increase in the amount of adsorbent dose from 0.2 to 2 g/L, the efficiency of boron removal increases. Considering the total cost of nanoparticles, an amount of 1 g/L was chosen as the optimal dose. This corresponds with a number of previous researches including a study of zinc ions removal using nZVI by Liang et al. [29] and an analysis of toxic metal hexavalent chromium removal using S-nZVI by Selvarani and Prema [30].



Element	Series	unn. C [wt.-%]	norm. C [wt.-%]	Atom. C [wt.-%]
Oxygen	K series	7.02	6.82	18.62
Sodium	K series	6.01	5.84	11.09
Sulfur	K series	3.52	3.42	4.66
Iron	K series	86.36	83.92	65.64

Fig. 4. An EDAX pattern of zero-valent iron nanoparticles modified by starch.

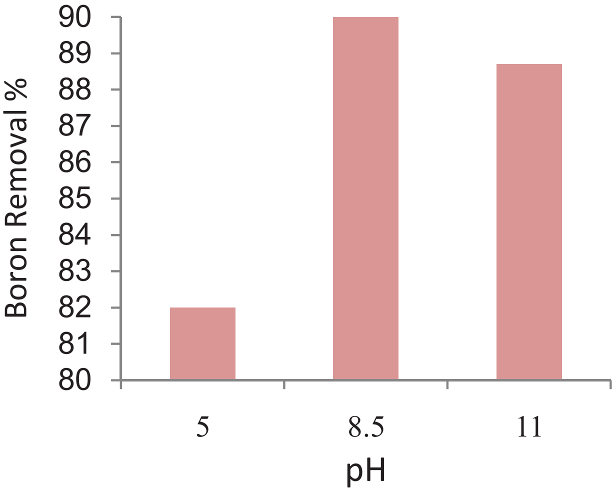


Fig. 5. The effect of pH on the efficiency of boron removal (initial boron = 10 mg/L, nZVI dose = 1 g/L, reaction time = 90 min).

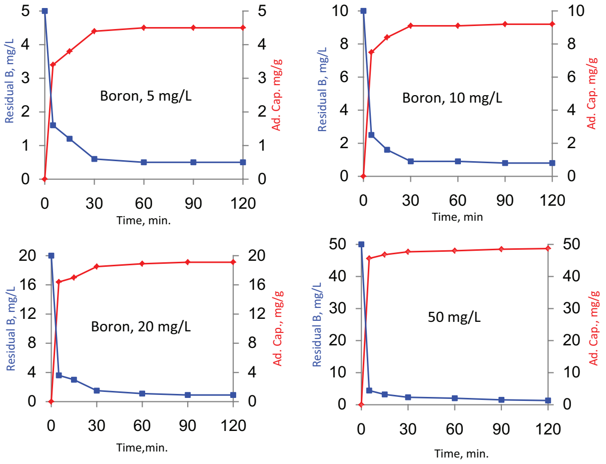


Fig. 6. The efficiency and adsorption capacity of S-nZVI at various boron concentrations (S-nZVI dose = 1 g/L, pH = 8.5).

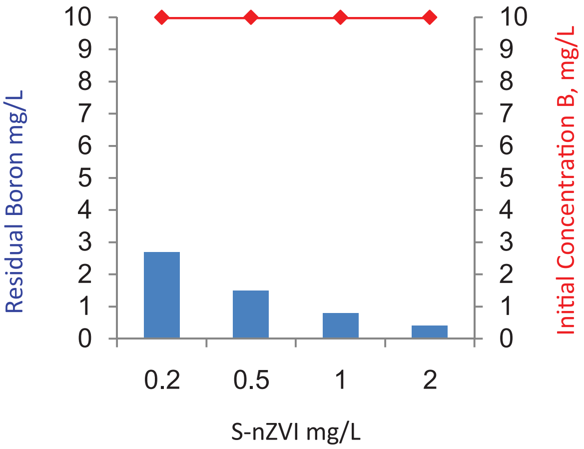


Fig. 7. The effect of S-nZVI dose on boron removal efficiency (initial boron = 10 mg/L, reaction time = 90 min, pH = 8.5).

Considering the reverse proportion of lag phase to nanoparticles concentration, by an increase in dose of nZVI, boron removal has increased. Therefore, by increasing the amount of adsorbent from 0.2 to 1 g/L, the efficiency of boron removal has increased from 73% to 92%. At low doses of nanoparticles, in addition to prolongation of lag phase, the limitation of active sites for adsorption causes a decline in efficiency.

3.4. Adsorption kinetics

Kinetic models introduce mechanism of adsorption and evaluation of adsorbent performance based on physical and chemical features of the adsorbent and the process of mass transfer. For correspondence between experimental data of boron adsorption by S-nZVI, we studied pseudo-second-order, Elovich, and intraparticle diffusion kinetic models [31,32]. The results showed that kinetic of boron adsorption by S-nZVI follows pseudo-second-order model ($R^2 = 0.999$).

According to Fig. 8 and based on pseudo-second-order kinetic equations, adsorptive capacity of boron by S-nZVI at equilibrium time fluctuates between 4.55 mg/g at initial concentration of 5 mg/L and 48.78 mg/g at initial concentration of 50 mg/L.

The correspondence between boron adsorption kinetics by nZVI and pseudo-second-order kinetic order proves the chemical adsorption of boron on the surface of nZVI [33]. Rajamohan and Al-Sinani [34] and Öztürk and Kavak [28] introduced the reaction of boron adsorption on clay and fly ash, respectively, based on pseudo-second-order kinetic order.

3.5. Adsorption isotherm

The study of adsorption isotherms determines the amount of adsorbate per unit mass of adsorbent at a certain temperature. These studies may be conducted by changing the concentration of adsorbate and maintaining the amount of adsorbent, or quite the opposite, by analyzing the adsorption rate of a certain concentration of the adsorbate by different amounts of the adsorbent [35]. In this study, we used Langmuir and Freundlich isotherms [31,32] for matching the experimental results. According to Fig. 6, by analyzing the changes in adsorption capacity of boron by S-nZVI vs. the reaction time, equilibrium time was determined as 30 min. The results showed that boron adsorption by S-nZVI is more consistent with Langmuir isotherm model ($R^2 = 0.93$). Accordingly, monolayer adsorption of boron on heterogeneous sites of S-nZVI having the separation factor of 0.59 is conducted favorably [36,37]. According to Fig. 9, the maximum adsorption capacity (q_m) of boron by S-nZVI was determined as 128.2 mg/g.

4. Conclusion

The efficiency of S-nZVI in removing 10 mg/L of boron at equilibrium time of 30 min was about 6% more than nZVI, so that S-nZVI obtained its maximum allowable concentration in drinking water about 1 h earlier than nZVI. Thus, starch can be used as a suitable and eco-friendly stabilizer for increasing the efficiency of nZVI in boron removal from aqueous solutions.

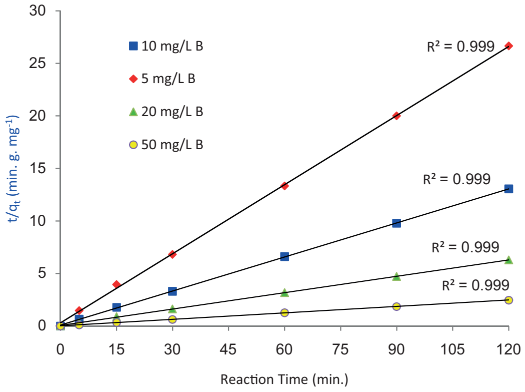


Fig. 8. Pseudo-second order kinetic curve for boron removal (pH = 8.5, adsorbent dose = 1 g/L).

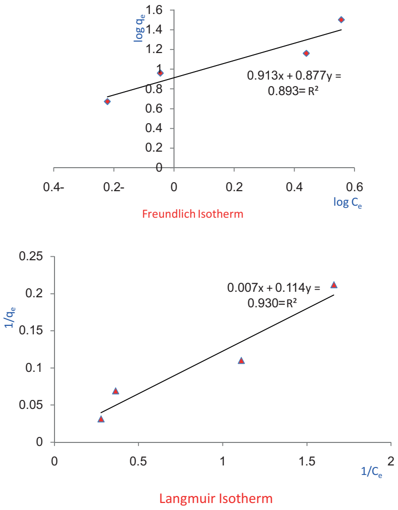


Fig. 9. Langmuir and Freundlich isotherms for boron removal by S-nZVI (initial boron = 10 mg/L, pH = 8.5, equilibrium time = 30 min, S-nZVI doses = 0.2, 0.5, 1, and 2 g/L).

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