



## Boron removal from aqueous solution by batch adsorption using Box–Behnken design

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### ABSTRACT

In the present study, boron sorption removal from aqueous solution by batch experiments was performed and the practicability of granular ferric hydroxide (GFH) for boron removal was studied. Box–Behnken experimental design method (BBD) was applied to the data for determination of the effects of important operating parameters such as initial boron concentration, pH, and dose of GFH on boron sorption efficiency. The obtained results from the present study suggested that BBD was an efficient and applicable method to obtain optimum conditions for boron removal from aqueous solution using GFH. The adsorption kinetic studies indicated that equilibrium was obtained as 20 h and about 96% boron removal efficiency was achieved in that time. The sorption process was well described by pseudo-second-order kinetic model. Freundlich isotherm represented a great fit to the data and was applicable model for the present study. Optimum pH and amount of GFH were calculated as 10 and 90 g L<sup>-1</sup> for maximum boron sorption efficiency. The results of the present study showed that GFH can be efficiently applied for boron removal from drinking water.

*Keywords:* Boron removal; Granular ferric hydroxide (GFH); Sorption isotherms; Box–Behnken design (BBD); Equilibrium and kinetic modeling

### 1. Introduction

Although boron is mostly presented in sea water and thermal spring water naturally, drinking and irrigation water sources can contain boron at different concentrations because of global usage of boron compounds. Boron compounds are useful for various industries include glass production, manufacture of pesticides, cosmetics, medicine, metal, and production of cleaning agent and disinfectants [1]. Moreover it is

migrated to the aquatic systems from natural process such as weathering of soils, rocks and sediments [2]. Boron is commonly presented in aquatic environments as boric acid and borate forms. However, they are found as widely water-soluble polyborates forms of B<sub>3</sub>O<sub>3</sub>(OH)<sub>4</sub><sup>-</sup>, B<sub>4</sub>O<sub>5</sub>(OH)<sub>4</sub><sup>-</sup>, and B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub><sup>-</sup> at high concentration of boron [3].

Boron is a necessary micronutrient for growth and functioning of plants, animals, and humans. Nevertheless both incompleteness and increment of boron in daily intake can induce several toxic effects and some-

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times death. Long-term utilization of water and food sources having high concentration of boron can cause important health problems including neurological effects, mental deficiency, cardiovascular disease, and reproductive disorders [4]. The guideline values of 2.4 and 1.0 mg L<sup>-1</sup> are represented for boron concentration in drinking water by World Health Organization and European Union, respectively. These identified values are provisional because boron removal from water is quite difficult using existing boron removal technologies [5]. Boron standard for drinking water is determined as 1.0 mg L<sup>-1</sup> by Turkish Standards 266-Water Intended for Human Consumption in Turkey. The natural fresh water and thermal water sources used for health, irrigation water, and drinking water purposes in Turkey especially in West Anatolia have much higher levels of boron concentrations than values given in national standards. Boron pollution in West Anatolia is originated from mostly natural areas because of the large boron reserves area in this region [6,7].

There is no global technique to reduce boron concentration below the related standards. Particularly at low boron concentrations, traditionally applied removal methods such as membrane filtration [8], ion selective resins [9], adsorption [10], electrocoagulation [3], and precipitation [11] can fail to satisfy. Adsorption for boron removal using cheap and easily attainable adsorbent is substantially beneficial, effective, economic, and quite easily applied method principally at low boron concentrations [10]. Up to the present, various adsorbents including aluminum-based water treatment residuals [12], calcareous soils [13], fly ash [10,14], goethite [2], magnesium oxide [15,16], magnetic particles [17], alumina [18], activated carbon [19], and calcined magnesite tailing [5] were evaluated for boron removal from aqueous solution. Granular ferric hydroxide (GFH) is a dominantly akaganeite material and recognized adsorbent for arsenate and arsenite removal [20]. GFH was capable of different pollutants removal from water include fluoride [21], natural organic matter [22], bromate [23], and perchlorate [24] as well as arsenic. Nevertheless, there is no study about boron removal from aqueous solution by adsorption using GFH as an adsorbent.

The statistical and mathematical experimental design methods provide to find the most suitable and explain independent variables combination to optimize the target function(s). These techniques also cause to reduce the number of the experiments, process cost, and required time for development of process installation [6].

The objective of the present study is to evaluate the boron removal from aqueous solution by GFH. The adsorption isotherms as well as adsorption kinet-

ics were investigated to identify the adsorption process. Factors affecting process which include initial boron concentrations, pH, and adsorbent amount were also examined using Box–Behnken experimental design method (BBD) to define the conditions of independent variables providing maximum boron removal efficiency. The obtained findings supplied an alternative adsorbent for boron removal and new perception for appropriateness of BBD for boron removal by adsorption.

## 2. Experimental

### 2.1. Materials

The stock solutions of boric acid (H<sub>3</sub>BO<sub>3</sub>) were prepared using the analytical grade Merck (Darmstadt, Germany) product. Boric acid solutions used in the batch adsorption experiments were freshly provided from stock solution using distilled water for dilution. pH values of the solutions were adjusted using HCl and NaOH solutions. GFH supplied from GEH-Wasserchemie (Germany) has particle size of 0.2–2.0 mm. The particle size distribution analysis was conducted for GFH material. The uniformity coefficient ( $d_{60}/d_{10}$ ) was calculated as about 3. The values of  $d_{10}$  and  $d_{90}$  were found as 0.3 and 1.6 from the particle size distribution curve, respectively. The median GFH diameter used for the adsorption experiments was determined as 0.71.

### 2.2. Adsorption experiments

The adsorptive removal of boron on GFH was carried out at room temperature (25 ± 2°C) by batch studies. The equilibrium studies were carried out at initial boron concentration of 100 mg L<sup>-1</sup>. For this purpose, 80 g L<sup>-1</sup> of GFH was added to 50 mL of boron solution and shaken at 150 rpm at various time duration for 24 h. Initial pH of solutions was adjusted to the intended value prior to addition of GFH. The suspension was centrifuged for 3 min at 7,500 rpm and then filtered using 0.45-µm pore size membrane filter to separate the solid phase from the suspension. The amount of the adsorbed boron on GFH was computed by the mass balance. All the experiments were realized in duplicate to measure experiment repeatability under the same circumstances and the average values were used in the present study.

### 2.3. Analytical methods

Initial and residual boron concentrations of the samples were analyzed using ICP-atomic emission

spectrometry (ICP-AES). The detection limit of ICP-AES was determined as 0.05 mg L<sup>-1</sup> for boron at the wavelength of 249.677 nm.

2.4. BBD and data analysis

For boron removal by adsorption using GFH, boron removal efficiency was the dependent variable (Y), while three substantial operation parameters that include amount of GFH, initial boron concentrations, and pH were taken into account as the independent variables. Initial boron concentration (X<sub>1</sub>) was varied between 1 and 100 mg L<sup>-1</sup>, while amount of GFH (X<sub>2</sub>) was ranged from 20 to 100 g L<sup>-1</sup>, and pH (X<sub>3</sub>) was ranged from 2 to 10. The three substantial operation parameters as well as their low, medium, and high levels are given in Table 1. The levels of the all independent variables were determined in terms of the results from preliminary experimental studies. A total of 17 experiments as listed in Table 2 were carried out and the Y was analyzed after each experiment. All the experiments were performed in duplicate and the obtained average Y was considered as the response. An empirical quadratic model (Y) (response function) for predicting the optimal point was in the following form:

$$Y = b_0 + \sum_{i=1}^k b_i X_i + \sum_{i=1}^k b_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^k b_{ij} X_i X_j \quad (1)$$

where Y is the boron removal efficiency (predicted response), k is the number of the input variables, X<sub>i</sub> and X<sub>j</sub> are the input variables, b<sub>0</sub> is the offset term, b<sub>i</sub> is the linear effect, b<sub>ii</sub> is the square effect, and b<sub>ij</sub> is the interaction effect. For the planning of the experiments, calculation of the coefficients, input test, and the drawing of the plots, the software Design Expert (Version 8.0.7.1, Stat-Ease Inc., Minneapolis, USA) was benefited. The validity and the reliability of the model

Table 1  
Variables in Box–Behnken design

Independent variables	Symbol coded	Range and levels		
		-1	0	+1
Initial boron concentration (mg L <sup>-1</sup> )	X <sub>1</sub>	1	50.5	100
Amount of GFH (g L <sup>-1</sup> )	X <sub>2</sub>	20	60	100
pH	X <sub>3</sub>	2	6	10

Table 2  
Box–Behnken design points and observed responses for boron sorption on GFH

Run	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	Boron sorption efficiency (%)	
				Observed	Predicted
1	1.0	20.0	6.0	0.00	0.25
2	50.5	60.0	6.0	42.85	40.70
3	50.5	60.0	6.0	38.28	40.70
4	50.5	20.0	10.0	6.10	9.49
5	1.0	60.0	2.0	10.20	12.36
6	100.0	20.0	6.0	25.30	24.08
7	50.5	60.0	6.0	39.48	40.70
8	50.5	60.0	6.0	41.08	40.70
9	50.5	20.0	2.0	4.30	1.89
10	100.0	100.0	6.0	63.10	62.85
11	50.5	100.0	2.0	11.40	8.01
12	50.5	100.0	10.0	92.70	95.11
13	1.0	100.0	6.0	52.00	53.23
14	1.0	60.0	10.0	56.10	52.46
15	100.0	60.0	10.0	78.60	76.44
16	50.5	60.0	6.0	41.80	40.70
17	100.0	60.0	2.0	18.20	21.84

were identified by checking the experimental and predicted values. In addition, the predicted boron removal efficiencies from response function were experimentally verified in an additional study.

3. Results and discussion

3.1. Effect of contact time and adsorption kinetics

In order to find out the equilibrium time and to realize sorption technique for maximum boron uptake, the sorption of boron on GFH was practiced as a function of contact time at initial boron concentration of 100 mg L<sup>-1</sup>, GFH dose of 80 g L<sup>-1</sup>, and pH value of 10. It was realized that boron removal efficiency increased with increasing time as demonstrated in Fig. 1. GFH exerted rapid initial uptake process followed by a slower kinetic to achieve a plateau. While boron removal efficiency was occurred about 82% within the 6 h, the equilibrium for adsorption was executed at 20 h with removal efficiency of about 96%. There was no significant increment in boron removal efficiency between 20 and 24 h.

Two kinetic models namely pseudo-first-order (PFO) and pseudo-second-order (PSO) were implemented in the present study to research adsorption technique and to estimate the adsorption rate of boron on GFH as shown in Fig. 1. The integrated shape of PFO kinetic model can be indicated in the following form:

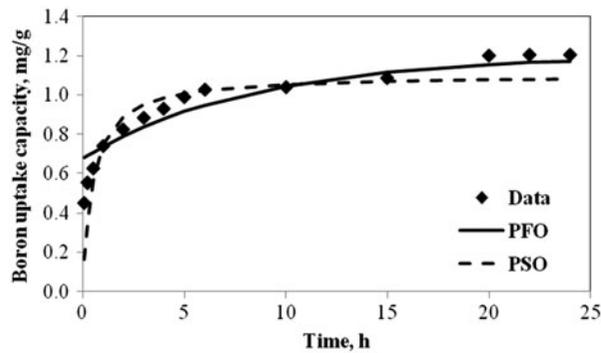


Fig. 1. Kinetic plot of boron adsorption onto GFH at GFH dose of  $80 \text{ g L}^{-1}$ , and initial boron concentration of  $100 \text{ mg L}^{-1}$ .

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (2)$$

where  $q_e$  and  $q_t$  are the amounts of boron adsorbed on the GFH at equilibrium and at time  $t$  (h), respectively, and  $K_1$  is the rate constant of PFO kinetic model ( $\text{h}^{-1}$ ). For initial boron concentration of  $100 \text{ mg L}^{-1}$ ,  $K_1$  and theoretical equilibrium sorption capacities  $q_e$  (calculated) were calculated by use of the slope and intercept of the linear plots of the  $\log(q_e - q_t)$  against  $t$  for GFH, respectively. The integrated shape of PSO kinetic model can be expressed in the following form:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where  $K_2$  is the rate constant for the PSO kinetic model ( $\text{g mg}^{-1} \text{ h}^{-1}$ ). For initial boron concentration of  $100 \text{ mg L}^{-1}$ ,  $q_e$  (calculated) and  $K_2$  were calculated by use of the slope and intercept of the linear plots of the  $t/q_t$  vs.  $t$  for GFH, respectively. The calculated kinetic parameters of PFO and PSO conjunction with correlation coefficients are listed in Table 3.

The obtained correlation coefficient for the PFO kinetic model was low. It implies that the PFO model was not fitted to the experimental data. Furthermore, the calculated  $q_e$  (cal) value for the PFO kinetic model was not found compatible with the experimentally obtained  $q_e$  (exp). This remarks that PFO model might not be adequate to identify the technique of boron sorption system onto the GFH. The correlation coefficient for the PSO kinetic model was higher than the PFO model. The obtained high correlation coefficient and comparatively closer  $q_e$  (cal) value to  $q_e$  (exp) for PSO show that the present boron sorption system on GFH can be described ideally by the PSO kinetic

Table 3

Kinetic parameters for the sorption of boron on GFH

Kinetic model	Value
PFO	
$q_e$ (exp) ( $\text{mg g}^{-1}$ )	1.200
$K_1$ ( $\text{h}^{-1}$ )	0.164
$q_e$ (cal) ( $\text{mg g}^{-1}$ )	0.526
$R^2$	0.846
PSO	
$q_e$ (exp) ( $\text{mg g}^{-1}$ )	1.200
$K_2$ ( $\text{g mg}^{-1} \text{ h}^{-1}$ )	1.891
$q_e$ (cal) ( $\text{mg g}^{-1}$ )	1.103
$R^2$	0.998

model. Furthermore, the parameter  $K_2$ , which corresponds to the velocity constant of PSO, is higher than the Lagergren rate constant of  $K_1$ . This fact shows that boron could be removed rapidly with GFH. For other adsorbents such as fly ash [7], calcined magnesite tailing [5], aluminum-based water treatment residual [12], activated carbon [25] used for boron removal from water, it was found that the PSO kinetic model was the most suitable model of explanation kinetic data for boron sorption.

### 3.2. BBD results

In order to evaluate the incorporated impact of process variables which include initial boron concentration, amount of GFH, and pH on the boron removal efficiency from aqueous solution, several experiments were carried out using BBD technic and obtained results along with predicted values are shown in Table 2. Four response models that include linear, interactive, quadratic, and cubic were managed to check the model sufficiency, and to determine the coefficients of the response equation. Various statistical tests such as sequential model sum of squares, lack of fit tests, and model summary statistics were applied to the data in the present study to decide the most suitable model among the above mentioned various models. Cubic model was not recommended for this system due to insufficient points to estimate the coefficients for this type of the model. Sequential model sum of squares and model summary statistics indicated that the quadratic model provided the best fit to the experimental data. Quadratic model was determined the most suitable model for predicting the boron removal efficiency because it provided the maximum  $R^2$  (0.9924), adjusted  $R^2$  (0.9826), and predicted  $R^2$  (0.8953) values along with low standard deviation (3.52) and  $p$ -values. Furthermore, the predicted

residual sum of squares (*press*) value of the quadratic model (1,197.34) was the smallest between the other applied forms of the model. *Press* is a measure of the fit of the model to the design points. Smaller values of *press* mean that the model better fits to the data. Consequently quadratic model was approved for further analysis.

The obtained second-order polynomial equation (Eq. (1)) with coefficients in term of actual factors for boron removal efficiencies (*Y*) using experimental data is given below:

$$Y = -16.67322 + 0.031629X_1 + 0.584218X_2 - 0.059683X_3 - 0.00179X_1X_2 + 0.018308X_1X_3 + 0.124219X_2X_3 + 1.33701 \times 10^{-3}X_1^2 - 0.00555X_2^2 - 0.19994X_3^2 \quad (4)$$

Boron sorption efficiencies on GFH ranged between 0 and about 93% as shown in Table 2. The predicted boron sorption values were calculated using Eq. (4). The value of  $R^2$  between the observed and predicted values was provided as quite high (0.992). The obtained high value of  $R^2$  suggested that the chosen model predictions are compatible substantially with the observed experimental results. At the same time, the high value of adjusted  $R^2$  (0.983) proved that only 0.017% of all the variations was not expressed by the chosen model.

The adequacy and significance of the selected quadratic model was evaluated by analysis of variance. The *p* values are used to predict if *F* value is large enough to remark statistical significance and used to explore the significance of each coefficient. *p* values lower than 0.05 indicate that the model and model terms are statistically significant. The model *F* value of 101.66 remarked that the model was significant at  $p < 0.0001$ . Therefore, the obtained second-order polynomial equation can properly be utilized to identify the boron sorption at the determined operation restriction. When *p* values of the model terms were taken into consideration to reveal the significance of the each coefficient, three linear coefficients, one quadratic, and one interactive coefficients as well as model itself were significant. Among all the terms, the linear effects of initial boron concentration ( $X_1$ ), amount of GFH ( $X_2$ ), and pH ( $X_3$ ) were found to be significant since the *p* values of them were found as  $< 0.0003$ . Similarly,  $X_2X_3$  was determined as significant interaction factor due to its low *p* value of  $< 0.0001$ . The quadratic term of  $X_2^2$  was also identified as significant factor due to its low *p* value of 0.0013. Although two cross-product coefficients and two interactive coefficients are not signifi-

cant, they are still considered in Eq. (4) because it is a hierarchical model. In addition, the *p* value of lack of fit (0.0418) in relation to *F* value of 7.36 implied that lack of fit was significant. The value of adequate precision was obtained as about 35 in the present study. Because a ratio greater than 4 is requested, there is an adequate signal. Therefore, the obtained statistical analysis results indicated that the chosen model is adequate to clarify the connection between independent and dependent factors and can be used for this sorption process.

The pH value of the aqueous environment is one of the most important parameter to control and understand the adsorption process and to clarify the influence of surface charge of the used adsorbent in adsorption process. Therefore, the adsorption of boron on GFH as a function of pH range of 2–10 was examined at GFH dose of  $80 \text{ g L}^{-1}$  and different initial boron concentrations and the obtained results are represented in Fig. 2. In the studied pH range, boron removal efficiency was raised by increased pH and maximum boron sorption efficiency was occurred at pH value of 10. While relatively low boron removal efficiencies were observed at low pH values, especially above pH values of 6 boron removal efficiencies were reached to remarkable values. This may be explained by the boron forms in the solution and surface charge of GFH. The boron forms in the aqueous solution show an alteration depending on the pH value of the solution. Accordingly, boron is at the form of boric acid ( $\text{B(OH)}_3$ ) at a pH lower than 7, while borate anions are presented especially at pH values between 6 and 11 [26]. Moreover GFH surface has negative charge at higher values of pH than 10 resulted in electrostatic repulsion forces between borate anion and GFH.

In the present study, the maximum boron removal efficiency observed at optimum pH value of 10 was realized about 70% at low initial boron concentration.

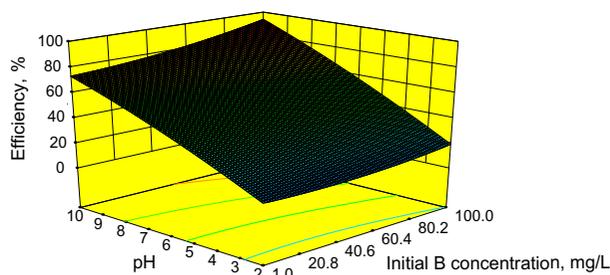


Fig. 2. Contour plot of the combined effects of pH and initial boron concentration on the boron removal efficiency at a constant GFH dose of  $80 \text{ g L}^{-1}$ .

On the other hand, boron removal efficiency was increased to above 90% at high initial boron concentrations. Consequently, initial boron concentration was found as the important and effective parameter for boron removal as shown by other researcher [1,27].

Determination of optimum adsorbent amount in adsorption processes is substantially important and fundamental in terms of preventing the consumption of excess amounts of adsorbent, reducing the process cost, and the regeneration of the adsorbent. The influence of the dose of GFH varied from 20 to 100 g L<sup>-1</sup> on the boron removal efficiency at the optimum pH value of 10 and different initial boron concentration is presented in Fig. 3. As expected adsorption percentage of boron on GFH increased with the increasing of dosage of GFH. The increment in the dose of GFH resulted in the rising of the surface area of adsorbent, adsorption sites for boron, and accordingly lowers residual boron concentration. But dose of GFH above 90 g L<sup>-1</sup> nebulously increased percentage boron sorption. It can be explained by reducing the boron concentration of the solution. It was found in the present study that sorption efficiency of boron onto the GFH increased from about 28 to 83% as the GFH amount increased from 40 to 90 g L<sup>-1</sup> for the initial boron concentration of 10 mg L<sup>-1</sup>, while raise in the efficiency was realized as from about 55 to 100% for the initial boron concentration of 100 mg L<sup>-1</sup>. In the low initial boron concentrations, the highest boron sorption efficiency was supposed relatively high GFH dose due to complexity in formation of adsorption bond between the boron and GFH in the solution. However for high initial boron concentrations, the highest boron sorption efficiency was observed slightly low GFH dose. Nevertheless, GFH was found as effective adsorbent for boron removal from aqueous solutions even at low boron concentrations.

Two experiments were executed to determine the reliability of the predicted model different from

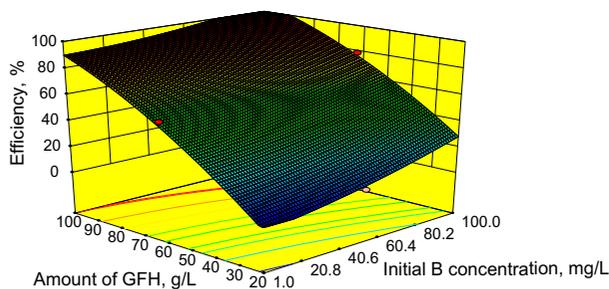


Fig. 3. Contour plot of the combined effects of dose of GFH and initial boron concentration on boron removal efficiency at optimum pH value of 10.

Box–Behnken design points and the results obtained from the model and experiments are checked in Table 4. Validation studies verified the predictions of the chosen model. Consequently, the chosen model was observed as a suitable, reliable, and powerful method for assessment of the optimum restrictions for boron removal on GFH by adsorption.

### 3.3. Adsorption isotherms

Isotherms of boron adsorption process onto GFH can be defined as the connection specified at a constant temperature between the amount of boron adsorbed per unit mass of GFH and the residual boron concentration in the aqueous solution. To identify the adsorption capacity of GFH for boron removal from water, the adsorption isotherms namely Freundlich and Langmuir isotherms were assessed. The isotherm experiments were conducted by dose of GFH varying between 20 and 90 g L<sup>-1</sup> at room temperature, and pH value of 10. The linear equations of Langmuir and Freundlich isotherms are demonstrated as follows:

$$\frac{M}{X} = \frac{1}{Q_{\max}} + \frac{1}{Q_{\max} \times k} \times \frac{1}{C_e} \quad (5)$$

$$\log \frac{X}{M} = \log K_f + 1/n \times \log C_e \quad (6)$$

where  $X/M$  is milligrams of boron adsorbed per gram of the GFH,  $C_e$  is boron concentration in the final solutions,  $Q_{\max}$  is Langmuir monolayer sorption capacity,  $k$  is Langmuir coefficient,  $K_f$  is Freundlich constant, and  $1/n$  is the Freundlich exponent coefficient. While Freundlich isotherm is empirical and quite applied model used to identify the heterogeneous systems and multi-layer adsorption onto GFH surface, Langmuir isotherm supposes that boron is adsorbed in a monolayer over a homogeneous GFH surface, there is a limited area available for boron adsorption onto GFH surface, and adsorption is reversible. The Langmuir and Freundlich isotherms and model constants for boron removal

Table 4

Comparison of the experimental and predicted results different from Box–Behnken design points

B concentration (mg L <sup>-1</sup> )	Dose of GFH (g L <sup>-1</sup> )	pH	Efficiency (%)	
			Observed	Predicted
40	70	8	54.65	57.58
70	80	9	79.25	77.53

using GFH are given in Fig. 4 and Table 5, respectively. Correlation coefficients ( $R^2$ ) for Langmuir and Freundlich isotherms for GFH were calculated as 0.917 and 0.984, respectively. Furthermore  $q_e$  (cal) values of Freundlich isotherm are more suited well with the  $q_e$  (exp). These results indicated that Freundlich isotherm represented a great fit to the data and is applicable model for the present study. The constant of  $K_f$  is relevant fundamentally to the capacity of the GFH for boron removal from aqueous solution. The constant of  $1/n$  is an indicator of robustness of adsorption bond. Larger values of  $K_f$  and smaller values of  $1/n$  in the present study proved that GFH has larger adsorption capacity and adsorption bond is quite strong between boron in the solute and GFH. At the same time, calculated values of  $K_f$  and  $1/n$  showed easy separation of boron from aqueous solution. Namely, the adsorption of boron on GFH was due to multilayer coverage of boron onto heterogenous solid surface. The batch maximum adsorption capacity of GFH according to Freundlich isotherm was calculated as  $1.025 \text{ mg g}^{-1}$ . The adsorption capacities of different adsorbents for boron removal from aqueous solution presented in the literatures were found as  $0.98 \text{ mg g}^{-1}$  for aluminum-based water treatment residuals [12],  $6.9 \text{ mg g}^{-1}$  for fly ash agglomerate [10],  $3.39 \text{ mg g}^{-1}$  for calcined alunite [6], and 1.965 for activated alumina [28].

Boron adsorptive removals from aqueous solutions on different adsorbents such as fly ash [10], functionalized chitosan [29], and silica-based adsorbent [30] were accorded with Freundlich isotherm model by

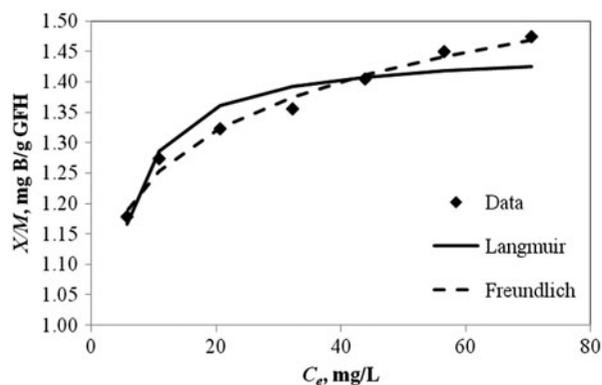


Fig. 4. Sorption isotherms of boron onto GFH.

Table 5  
Isotherm parameters of boron sorption onto GFH at 25°C

Freundlich			Langmuir		
$K_f$	$1/n$	$R^2$	$Q_{max}$	$k$	$R^2$
1.025	0.0846	0.984	1.453	0.710	0.917

some researchers. Otherwise, Langmuir isotherm model was notified to accord well boron removal using other adsorbents namely aluminum-based water treatment residual [12], calcareous soil [13], magnesium oxide [16], calcined magnesite tailing [5], iron oxide [31]. Boron adsorption onto tannin gel was found as compatible both Freundlich and Langmuir isotherm models by Morisada et al. [27].

#### 4. Conclusions

Boron adsorption from aqueous solutions using GFH was examined in the present study by batch experiments and the following conclusions are reached:

- Equilibrium time to achieve the maximum boron removal by GFH was obtained as 20 h. At equilibrium time, boron adsorption capacity was realized as  $1.2 \text{ mg g}^{-1}$  while obtained maximum removal efficiency was about 96%.
- Maximum boron removal efficiency from aqueous solution onto GFH was found at pH value of 10 using Box–Behnken experimental design method.
- From the results of statistical design, boron removal efficiency increased with increasing dose of GFH. When the amount of GFH was increased from 20 to  $90 \text{ g L}^{-1}$ , boron adsorption efficiency raised from approximately 28 to 100% for initial boron concentration of  $100 \text{ mg L}^{-1}$ .
- Kinetic results revealed that the sorption process can be clarified more conveniently by the PSO model.
- Freundlich isotherm represented a great fit to the data and was applicable model for the present study.
- The obtained results suggested that Box–Behnken design method was efficient and applicable method for identification the optimum circumstances for boron removal by adsorption method by GFH.
- The results obtained from the present study demonstrated that GFH is an influential, dependable, and cost-effective adsorbent for boron from aqueous solution, in addition to the high removable efficiency. Therefore, GFH can be approved as alternative and acceptable adsorbents and has potential usage for boron removal.
- The obtained results of statistical experiments designs can be exploited to lead, guide, and conduct the pilot scale and full scale studies about boron removal from drinking water using GFH.

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