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# Removal of boron from aqueous solution by adsorption on Al<sub>2</sub>O<sub>3</sub> based materials using full factorial design

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## Abstract

This paper aims the adsorption of boron from aqueous solution onto Siral 30 and Pural using 2<sup>3</sup> full factorial design. The effect of individual variables and their interactional effects for boron adsorption were also determined. From the statistical analysis, it is inferred that as pH and temperature increased boron adsorption from aqueous solution decreased. Siral 30 was found to be more efficient adsorbent than Pural. The unimportant factor affecting boron adsorption from aqueous solution was also verified by using Fisher adequacy test. At the 90% confidence level, the type of adsorbent, temperature and type of adsorbent–temperature interaction was effective on boron adsorption from aqueous solution. The experimental results were fitted to the Langmuir, Freundlich and Dubinin–Radushkevich (DR) equations to find out adsorption capacities. In most cases, the results indicate that Freundlich and DR equations are well described with the sorption data. The adsorption capacity values of Siral 30 calculated from Freundlich and DR equation was greater than that of Pural. The thermodynamic parameters were also estimated and the adsorption process was not spontaneous nature.

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# 1. Introduction

Turkey possesses approximately 60% of the world's boron reserves. The known borate reserves in Turkey are located in four main districts, namely Emet, Bigadiç, Kırka and Mustafakemalpaşa (Kestelek) [1,2]. Annually, 175,000 tonnes of borax sludge forms during production in the borax concentration unit and borax pentahydrate unit of the Etibank Kırka Borax plant in Turkey. This waste, containing 19.44% B<sub>2</sub>O<sub>3</sub> is discharged into the ponds having an area bigger than the plant area. Boron compounds in this waste pass to soil; they form some complexes with heavy metals so that the potential toxicity of heavy metals increases. Thus, boron compounds cause some serious health and environmental problems, when the complexes pass to groundwater [3]. Boron(III) has virulence for reproduction and causes disease of the nervous system [4]. Boron is a micronutrient element that can be toxic to plants at elevated concentrations. In arid regions, additions of B via the irrigation

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water often lead to toxicity symptoms and yields reduction [5]. Therefore, boron must be removed from water and wastewater.

There are a lot of methods for the removal of boron from waters and wastewaters. These are adsorption on Chitosan Resin modified by saccarides [6], adsorption on waste sepiolite and activated waste sepiolite [2], adsorption by cell walls [5], removal by *N*-methylglucamine-type cellulose derivatives, ion-exchange resin [7] and crosslinked polymer gels [8].

It is known that pH of solution is one of the most important factor affecting boron adsorption on clays. It can be said that the amount of adsorbed boron is lower at low pH values. In addition to this, the amount of boron increased by increasing solution of pH. Acidic materials may not be suitable adsorbent for boron removal. Therefore more basic adsorbents can be chosen for the removal of boron from aqueous solution.

The technique of statistical design for experiments can be used for process characterization, optimization and modeling. It has been widely accepted in manufacturing industry for improving product performance and reliability, process capability and yield. In the statistical design experiments, the factors involved in an experiment at their respective levels, were simultaneously varied. Thus, a lot of information can be taken with a minimum

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Table 1 The properties of Siral 30 and Pural

Sample	Pural	Siral 30
SiO <sub>2</sub> content (%)	-	28
$Al_2O_3$ content (%)	76	72
BET area $(m^2 g^{-1})$	250	467
Density $(g m L^{-1})$	0.70	0.34
Particle size distribution (%)		
<25 µm	25.3	26.9
<45 µm	50.6	52.1
< 90 µm	93.3	94.0

number of experiment trials [2,9–12]. The experiments in which the effects of more than one factor on response are investigated are known as full factorial experiments. The most important advantages are that not only the effects of individual parameters but also their relative importance in given process are obtained and that the interactional effects of two or more variables can also be known. This is not possible in a classical experiment [13,14,3].

In this study, adsorption and desorption of boron from aqueous solution onto Pural and Siral 30 was investigated. Two level factorial designs were used to determine the effects of the parameters and their interactions on boron removal by batch adsorption method. It will be also determined which one of the most important factor affecting boron is. Classical experiments were also conducted to find out the adsorption capacities of adsorbent and the mean free energy values of adsorption process which are used for the determination of the type of adsorption.

## 2. Materials and methods

Pural and Siral 30 samples were received from Condea AG/Germany. The compositions, surface areas and the pore size distribution of the samples are summarized in Table 1. It is noticeable that the contents of SiO<sub>2</sub> (%) and Al<sub>2</sub>O<sub>3</sub> (%) of the samples were the basic difference. The samples were dried at 383 K for 2 h before being used. Boric acid which was supplied from Merck was used without treatment. Boric acid stock solution (50 mg L<sup>-1</sup>) was prepared by dissolving it in the distilled water. Further solutions were freshly prepared from stock solution for each experimental run.

0.1 g adsorbent was used for boron adsorption experiments. The samples were mixed with 25 mL aqueous solutions of different concentrations of boric acid for 3 h and kept under a constant speed 200 rpm in an isothermal shaker at studied temperature unless otherwise stated. After adsorption, samples were centrifuged at 4000 rpm for 15 min and the amount of boron in supernatant analyzed using Shimadzu UV–vis Spectrophotometer by Azomethine-H method [15]. The pH of the boric acid suspensions were adjusted with 0.1 M NaOH using a pH meter. The amount of boron adsorbed on Pural and Siral 30 were found by subtracting the final solution concentration from initial concentration of boron solutions.

For the desorption study, boron loaded Siral 30 and Pural were subjected to shaking at 200 rpm with 25 mL of distilled water at about pH 6. Desorbed boron was determined as mentioned above.

The principle steps of statistically designed experiments are determination of response variables, factors and factor levels; choice of the experimental design; statistical analysis of the data.  $2^3$  factorial designs were selected in our study. It indicates that for quantification of the effects of the three variables on boron adsorption, a two level factorial design of experiments was applied. The variables used in our work are adsorbent type (Siral 30, Pural), pH of the solution (5.7, 9.5) and temperature (298 K and 313 K). The number of experiments conducted is considered as  $2^3$ . The two levels which correspond to each variable are taken in coded form as +1 and -1.

In this study, the sorption of boron onto Siral 30 and Pural were evaluated by three isotherms, namely Langmuir, Freundlich and Dubinin–Radushkevich (DR). Linear regression method was used to find the isotherm constants. Due to inherent bias resulting from linearization, alternative isotherm parameters were found by nonlinear regression. This provides a mathematically rigorous method for determining isotherm parameters using the original form of the equation. These parameters were determined from the linear form of Langmuir and the original form of equation fitted using SigmaPlot version 4 [16].

## 3. Results and discussion

## 3.1. Statistical analysis

Since the experimental design involves three variables at two levels (low and high), the factorial of the type  $2^3$  has been applied. Each experiment was done duplicate. The variables and levels for the experiment were presented in Table 2.

The higher level was designated as (+) and the lower value was designated as (-). As can be seen from Table 2,  $x_1$ ,  $x_2$  and  $x_3$ show the levels of adsorbent type, pH and temperature, respectively.  $X_1$ ,  $X_2$  and  $X_3$  represent the coded forms of adsorbent type, pH and temperature as previous one. The experimental design matrix for boron adsorption from aqueous solution was given in Table 3. While Y is showing the amount of boron adsorbed (response), the regression equation with three parameters and

Table 2

Actual and vis-à-vis coded values of parameters in 2<sup>3</sup> full factorial design for boron adsorption

Level of variables	Adsorbent type		pH of solution		Temperature (K)	
	Actual $(x_1)$	Coded $(X_1)$	Actual $(x_2)$	Coded $(X_2)$	Actual ( <i>x</i> <sub>3</sub> )	Coded (X <sub>3</sub> )
First level	Siral 30	_	5.70	_	298	_
Second level	Pural	+	9.5	+	318	+

 Table 3

 Experimental design matrix for boron adsorption from aqueous solution

Experiment no. Adsorbent ty Actual $(x_1)$	Adsorbent type		pH of solution		Temperature (K)		Response $(Y_i)$	
	Actual $(x_1)$	Coded $(X_1)$	Actual $(x_2)$	Coded $(X_2)$	Actual $(x_3)$	Coded $(X_3)$		
1	Siral 30	_	5.70	_	298	_	$Y_1$	$Y_9$
2	Pural	+	5.70	_	298	_	$Y_2$	$Y_{10}$
3	Siral 30	_	9.50	+	298	_	$Y_3$	$Y_{11}$
4	Pural	+	9.50	+	298	_	$Y_4$	$Y_{12}$
5	Siral 30	_	5.70	_	318	+	$Y_5$	$Y_{13}$
6	Pural	+	5.70	_	318	+	$Y_6$	$Y_{14}$
7	Siral 30	_	9.50	+	318	+	$Y_7$	$Y_{15}$
8	Pural	+	9.50	+	318	+	$Y_8$	Y <sub>16</sub>

Table 4

Trial	<i>X</i> <sub>1</sub>	<i>X</i> <sub>2</sub>	<i>X</i> <sub>3</sub>	$X_1 X_2$	<i>X</i> <sub>1</sub> <i>X</i> <sub>3</sub>	<i>X</i> <sub>2</sub> <i>X</i> <sub>3</sub>	$X_1 X_2 X_3$	Y adsorbed Boron amount $(mg L^{-1})$	Y adsorbed Boron amount $(mg L^{-1})$	Y average adsorbed Boron amount $(mg L^{-1})$
1	_	_	_	+	+	+	_	0.471	0.551	0.511
2	+	_	_	_	-	+	+	0.606	0.594	0.600
3	_	+	_	_	+	_	+	0.471	0.563	0.517
4	+	+	_	+	-	-	_	0.594	0.557	0.576
5	_	_	+	+	_	_	+	0.361	0.348	0.355
6	+	_	+	_	+	_	_	0.557	0.551	0.554
7	_	+	+	_	_	+	_	0.102	0.373	0.238
8	+	+	+	+	+	+	+	0.514	0.533	0.524

their interaction with each other can be given with the following expression [17,2]

$$Y_{i} = b_{0} + b_{1}X_{1i} + b_{2}X_{2i} + b_{3}X_{3i} + b_{12}X_{1i}X_{2i} + b_{13}X_{1i}X_{3i} + b_{23}X_{2i}X_{3i} + b_{123}X_{1i}X_{2i}X_{3i}$$
(1)

The regression coefficients are computed as below

$$b_0 = \sum \frac{Y_i}{N} \tag{2}$$

$$b_j = \sum \frac{X_{ji}Y_i}{N} \tag{3}$$

$$b_{nj} = \sum \frac{(X_{nj}X_{ji})Y_i}{N} \tag{4}$$

where  $X_{ji}$  values (j = 1, 2, 3; i = 1, 2, 3, ..., 16) indicate the corresponding parameters in their coded forms;  $b_0$  the average value of the result;  $b_1$ ,  $b_2$  and  $b_3$  the linear coefficients;  $b_{12}$ ,  $b_{13}$ ,  $b_{23}$  and  $b_{123}$  represent the interaction coefficients. *N* is the number of total experiments conducted.

For boron adsorption from aqueous solution, coefficients  $b_1$ ,  $b_2$  and  $b_3$  show the effect of adsorbent type, pH and temperature respectively. Coefficients  $b_{12}$ ,  $b_{13}$  and  $b_{23}$  show the interacting effects of adsorbent type–pH, adsorbent type–temperature and pH–temperature respectively. Coefficient  $b_{123}$  which implies the interacting effect of adsorbent type–pH–temperature represents the interacting effect of all three variables. The design of trial runs (in coded form) for boron adsorption from aqueous solution was summarized in Table 4. The values of regression coefficients obtained are presented in Table 5. When the results calculated

from the trial runs are incorporated in the regression Eq. (5) can be shown as

$$Y = 0.4840 + 0.0790X_1 - 0.0206X_2 - 0.0666X_3$$
  
+0.0071X\_1X\_2 + 0.0421X\_1X\_3 - 0.0161X\_2X\_3  
+0.0146X\_1X\_2X\_3 (5)

This equation reveals the effect of individual variables and interactional effects for boron adsorption from aqueous solution. As can be seen from Eq. (5), adsorbent type has a positive effect, while pH and temperature of solution has a negative effect on the boron removal from aqueous solution in the range of variation of each variable selected for our work. On the one hand, the greatest effect on boron removal was supplied by adsorbent type. Temperature and adsorbent type–temperature are following the effect of adsorbent. On the other hand, the adsorbent type–pH has the least effect. All of the parameters have an influence on the boron removal by adsorption. The effects of pH and temper-

Table 5	
Values of model coefficients	

Main and interaction coefficient	Values		
$\overline{b_0}$	0.4840		
$b_1$	0.0790		
$b_2$	-0.0206		
<i>b</i> <sub>3</sub>	-0.0666		
$b_{12}$	0.0071		
$b_{13}$	0.0421		
$b_{23}$	-0.0161		
$b_{123}$	0.0146		

Table 6Analysis of variance F ratios and decisions

Source of variation	F ratio	Decision				
		$\alpha^1 = 0.1$	$\alpha^1 = 0.05$	$\alpha^1 = 0.01$		
$\overline{X_1}$	17.73	Effective	Effective	Effective		
$X_2$	1.22	Ineffective	Ineffective	Ineffective		
$X_3$	12.62	Effective	Effective	Effective		
$X_1X_2$	0.14	Ineffective	Ineffective	Ineffective		
$X_1X_3$	5.06	Ineffective	Ineffective	Effective		
$X_2X_3$	0.74	Ineffective	Ineffective	Ineffective		
$X_1 X_2 X_3$	0.61	Ineffective	Ineffective	Ineffective		

 $\alpha^1$ : probability level.

ature have a negative values, indicating that the amount of boron adsorbed decreased while the factor varied from low level to its high level [18,2].

The importance of each factor was determined by the *F* test method [2,3,19–21]. Thus, unimportant factor affecting boron adsorption from aqueous solution can also be justified. The fit of the regression equations with the observations was tested through Fisher's adequacy test at the 90%, 95% and 99% confidence level. The *F* ratios were computed according to variance analysis of data. *F* ratios and decisions were summarized in Table 6. When the *F* values estimated were compared with Fisher's value  $[F_{0.1}(1,8)] = 3.46$ ;  $[F_{0.05}(1,8)] = 5.32$ ;  $[F_{0.01}(1,8) = 11.26]$ . At the 90% confidence level,  $X_1$ ,  $X_3$  variables and  $X_1X_3$  interaction was effective on boron adsorption from aqueous solution. Moreover, at the 99% and 95% confidence level,  $X_1$  and  $X_3$  are found to be effective. In addition to this, it can be assumed that the following equation was adequate at the 90% confidence level.

$$Y = 0.484 + 0.079X_1 - 0.0666X_3 + 0.0421X_1X_3 \tag{6}$$

However, at the 95% and 99% confidence level the equation can be written as below

$$Y = 0.484 + 0.079X_1 - 0.0666X_3 \tag{7}$$

As was presented in Table 6, the most important parameter which is efficient in boron adsorption from aqueous solution can be obtained to be type of adsorbent, which is followed by temperature of solution. The interaction between type of adsorbent and temperature was an important factor affecting boron adsorption. The interaction between type of adsorbent and pH was the least important factor for boron adsorption. From the statistical analysis, it can be concluded that adsorption was unfavoured by an increase in pH and temperature. Siral 30 was more effective than Pural for boron adsorption from the aqueous solution.

#### 3.2. Adsorption isotherms

The adsorption isotherms of boron adsorption on Siral 30 and Pural were depicted in Fig. 1. According to the shapes of the curves, the isotherms corresponding to boron adsorption onto Siral 30 at 298 K and Pural at 318 K, may be classified as S type of the Giles classification [22]. The S type isotherm suggests

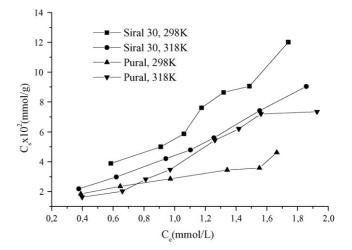


Fig. 1. Adsorption isotherms for boron sorption on Siral 30 and Pural.

cooperative adsorption, which operates if adsorbate-adsorbate interaction is stronger than adsorbate-adsorbent interaction. The clustering of adsorbate molecules at the surface is favored because they bond more strongly with one another than with the surface [23]. However the isotherms corresponding to boron adsorption onto Pural at 298 K may be considered as L type of the Giles classification, reflecting a relatively high affinity between boron species and Pural. This also indicates that no strong competition occurs for the adsorption sites between solvent molecules and adsorbate molecules. The isotherm for boron adsorption onto Siral 30 at 318 K may be classified as C type of Giles classification, this fact implying that low range of adsorption was observed at that temperature. It also shows a constant relative affinity of the adsorbate molecules for Siral 30 at 318 K. It is known that C type isotherm is an indicative of physical adsorption.

One should keep in mind that the isotherm shapes themselves can never prove the adsorption mechanism; they can only provide a reasonable mechanism for adsorption. It can be added that adsorption mechanism must be proved by molecular spectroscopy, the other isotherm equations such as Dubinin–Radushkevich (DR) equation and thermodynamic parameters.

## 3.2.1. Langmuir isotherm

The Langmuir isotherm, which is valid for monolayer sorption onto a surface with a finite number of identical sites and uniform adsorption energies is given by the equation [24]. Nonlinear form of Langmuir equation can be expressed by the following equation:

$$C_{\rm s} = \frac{K_{\rm L} C_{\rm m} C_{\rm e}}{1 + L C_{\rm e}} \tag{8}$$

where  $C_{\rm m}$  is the amount of adsorption corresponding to monolayer coverage (mmol g<sup>-1</sup>),  $C_{\rm e}$  the equilibrium concentration of boron solution and  $C_{\rm s}$  is the amount of boron adsorbed (mmol g<sup>-1</sup>). *L* is a constant related to adsorption energy. The

Table 7
Isotherm constants for boron adsorption onto Siral 30 and Pural at 298 K

	Siral 30	Pural
Fitted Langmuir		
$C_{\rm m} ({\rm mmol}{\rm g}^{-1})$	-0.093	0.075
L	-0.324	0.719
R	0.812	0.951
Linear form of Langmuir		
$C_{\rm m}  ({\rm mmol}  {\rm g}^{-1})$	-0.800	0.116
L	-0.071	0.393
R	0.032	0.666
Fitted Freundlich		
$K_{\rm f} ({\rm mmol}{\rm g}^{-1})$	0.046	0.031
n <sub>f</sub>	1.661	0.603
R	0.795	0.959
Linear form of Freundlich		
$K_{\rm f} ({\rm mmol}{\rm g}^{-1})$	0.057	0.031
n <sub>f</sub>	1.327	0.565
R	0.986	0.976

Table 8

Isotherm constants for boron adsorption onto Siral 30 and Pural at 318 K

	Siral 30	Pural
Fitted Langmuir		
$C_{\rm m}  ({\rm mmol}  {\rm g}^{-1})$	-2.996	-0.860
L	-0.411	-0.044
R	0.857	0.970
Linear form of Langmuir		
$C_{\rm m}  ({\rm mmol}  {\rm g}^{-1})$	0.883	-0.297
L	0.056	-0.115
R	0.283	0.425
Fitted Freundlich		
$K_{\rm f} ({\rm mmol}{\rm g}^{-1})$	1.666	0.039
$n_{\rm f}$	2.884	1.099
R	0.913	0.973
Linear form of Freundlich		
$K_{\rm f} ({\rm mmol}{\rm g}^{-1})$	0.045	0.037
n <sub>f</sub>	1.047	1.474
R	0.993	0.999

nonlinear form of Langmuir equation can be linearized as below:

$$\frac{C_{\rm e}}{C_{\rm s}} = \frac{1}{C_{\rm m}L} + \frac{C_{\rm e}}{C_{\rm s}} \tag{9}$$

 $C_{\rm m}$  and *L* were calculated from the slope and intercept of Langmuir plots of  $C_{\rm e}/C_{\rm s}$  versus  $C_{\rm e}$ . The results were listed in Tables 7 and 8. Based on these *R*-values, the Langmuir equation did not provide an accurate description of the experimental data. However, the fit of nonlinear form of Langmuir equation has a better level of conformity than linear form of Langmuir equation.

#### 3.2.2. Freundlich equation

Freundlich equation is employed for boron adsorption from aqueous solution. The Freundlich equation is applied to describe heterogeneous systems and reversible adsorption and is not restricted to the formation of monolayer [25]. It describes reversible adsorption [26]. The Freundlich adsorption isotherm has the form of

$$C_{\rm s} = K_{\rm f} C_{\rm e}^{n_{\rm f}} \tag{10}$$

where  $C_s$  is the equilibrium boron concentration on adsorbents  $(\text{mmol g}^{-1})$  and  $C_e$  is the equilibrium boron concentration in solution  $(\text{mmol L}^{-1})$ . The  $n_f$  values are indicative of adsorption intensity.  $K_f$  is considered as relative adsorption capacity  $(\text{mmol g}^{-1})$ . This equation can be rearranged to the following linear form.

$$\ln C_{\rm s} = \ln K_{\rm f} + n_{\rm f} \ln C_{\rm e} \tag{11}$$

When the sorption data were analyzed according to Eq. (11), a plot of  $\ln C_{\rm s}$  versus  $\ln C_{\rm e}$  enables to determine the values of  $n_{\rm f}$ and  $K_{\rm f}$ . The results were presented in Tables 7 and 8. The fit of Freundlich equation for the adsorption of boron on Siral 30 and Pural was good where the *R* values of the linear regression determined was greater than 0.976. Based on R values, for boron adsorption onto Siral 30 and Pural, linear form of Freundlich equation seems to produce a better fit in comparison with linear form of Langmuir. As observed from Tables 7 and 8, the fit of linear form of Freundlich equation is better than nonlinear form with the experimental data of boron sorption. The constant is also known a measurement of linearity. If  $n_{\rm f}$  is equal to unity, the adsorption is linear and adsorption sites are homogenous in energy and no interaction takes place between the adsorbed species. If the value of  $n_{\rm f}$  smaller than 1, adsorption is favorable. It shows that the sorption capacity increases and new adsorption sites occur. If the value of  $n_{\rm f}$  is greater than 1, adsorption bond becomes weak; unfavorable adsorption occurs as a result of the adsorption capacity decreases [27-29].

As can be seen from the linear fit of Freundlich equation in Tables 7 and 8, boron adsorption onto Pural at 318 K and onto Siral 30 at 298 K and 318 K was unfavorable. It is also observed that  $K_f$  value is increasing with the rise in the temperature from 298 K to 318 K for boron adsorption onto Pural samples. However  $K_f$  values are decreasing with the increase in temperature from 298 K to 318 K for Siral 30. In the temperature range of 298 K and 318 K,  $n_f$  value is increasing for Pural sample.

## 3.2.3. DR isotherm

A popular equation for the analysis of a high degree of rectangularity is proposed by Dubinin and Radushkevich [30,31]. In DR isotherm, the equation used for adsorption type can be given as below:

$$\ln C_{\rm s} = \ln X_{\rm m} - k\varepsilon^2 \tag{12}$$

where  $\varepsilon$  (polanyi potential) is  $RT \ln(1 + 1/C_e)$ ,  $C_e$  the equilibrium concentration of boron in solution (mol L<sup>-1</sup>) and  $C_s$  is the equilibrium concentration of boron on adsorbents (mol g<sup>-1</sup>).  $X_m$  is the adsorption capacity (mol g<sup>-1</sup>) and R is the gas constant  $8.314 \times 10^{-3}$  kJ mol<sup>-1</sup> K<sup>-1</sup>. T is the temperature (K).

The value of k is a constant and is used to calculate adsorption energy (mol<sup>2</sup> kJ<sup>-2</sup>). Plots of ln  $C_s$  versus  $\varepsilon^2$  yields a straight line of slope k and intercept ln  $X_m$ . Plotting the left hand side of Eq. (12) against  $\varepsilon^2$  yields a straight line of slope k and inter-

Table 9 DR isotherm constants for boron adsorption onto Siral 30 and Pural

	Pural		Siral 30		
	298 K	318 K	298 K	318 K	
R	0.974	0.971	0.986	0.990	
$X_{\rm m} ({\rm mol}{\rm g}^{-1})$	0.00021	0.00262	0.00660	0.00176	
k	0.00647	0.01274	0.01621	0.01093	
$E (kJ mol^{-1})$	-8.791	-6.265	-5.554	-6.764	

cept,  $\ln X_{\rm m}$ . The results were given in Table 9. As observed from Table 9, adsorption capacity values are increasing with the increase of temperature from 298 K to 318 K for Pural sample.

The mean free energy change of adsorption (E) can be calculated using the following expression

$$E = -(2k)^{-0.5} \tag{13}$$

The magnitude of *E* can be used for estimating the type of adsorption. According to [32], the magnitude of *E* is between  $8 \text{ kJ mol}^{-1}$  and  $16 \text{ kJ mol}^{-1}$ , adsorption type can be explained by ion-exchange. It is accepted that when the adsorption energy is lower than  $8 \text{ kJ mol}^{-1}$ , the type of adsorption can be considered as physical adsorption [33,34]. From the Table 9, it can be inferred that the type of adsorption can be generally described as physisorption.

## 3.2.4. Thermodynamic parameters

In order to evaluate the feasibility and the effect of temperature better, for boron adsorption onto Siral 30 and Pural, thermodynamic parameters such as standard free energy change  $(\Delta G^{\circ})$ , standard enthalpy change  $(\Delta H^{\circ})$  and standard entropy change  $(\Delta S^{\circ})$  were also obtained. The Gibbs free energy change of adsorption process was calculated by using the following equations

$$\Delta G^{\circ} = -RT \ln K_{\rm c} \tag{14}$$

$$K_{\rm c} = \frac{C_{\rm s}}{C_{\rm e}} \tag{15}$$

where  $K_c$  is the equilibrium constant,  $C_s$  the amount of boron adsorbed (mmol g<sup>-1</sup>),  $C_e$  is the equilibrium concentration (mmol L<sup>-1</sup>) of boron in the solution. *T* is the solution temperature and *R* is the gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>).

Standard enthalpy change  $(\Delta H^{\circ})$  and  $\Delta S^{\circ}$  values of adsorption can be calculated from van't Hoff equation given as below

$$\ln K_{\rm c} = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT}$$
(16)

Table 10

Thermodynamic parameters for the uptake of boron on Siral 30 and Pural

Table	11	
raute	11	

Desorption values for Pural and Siral samples in 0.1 M HCl and distilled water

Samples	HCl (%)	Distilled water (%)	
Pural	35.2	42.5	
Siral	>1	>1	

The values of  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  were estimated from the slope and intercept of the plot of  $\ln K_{\rm c}$  against 1/T.

When the temperature increased from 298 K to 318 K,  $\Delta G^{\circ}$  is increased from 7.628 kJ mol<sup>-1</sup> to 9.860 kJ mol<sup>-1</sup> for Pural and from 7.854 kJ mol<sup>-1</sup> to 8.319 kJ mol<sup>-1</sup> for Siral 30 respectively. As presented in Table 10, the positive of  $\Delta G^{\circ}$  values at given temperatures indicates the nonspontaneous nature of the adsorption. The positive values of  $\Delta G^{\circ}$  do not confirm the feasibility of the adsorption process. The negative value of standard enthalpy change for boron adsorption on Pural implies the exothermic adsorption. However, the positive value of standard enthalpy change for boron adsorption process. Negative  $\Delta S^{\circ}$  values for boron adsorption process. Negative  $\Delta S^{\circ}$  values for boron adsorption onto Siral 30 and Pural indicate a decrease in degree of freedom of the boron species.

## 3.2.5. Desorption

Boron desorption was measured by immersing the boron loaded Siral 30 and Pural samples into distilled water and 0.1 M HCl, shaking 200 rpm and at 298 K. The duration of desorption was similar to adsorption time. The desorption values for Pural and Siral samples are summarized in Table 11. Boron desorption values for Pural samples are 42.5% and 35.2% in distilled water and 0.1 M HCl respectively. However, desorption of boron from boron loaded Siral 30 in distilled water and 0.1 M HCl was very low level, less than 1%. This is indicative of physical attraction between boron species and Pural. Besides, attraction between boron species and Siral sample may be greater than that of Pural sample due to low desorption values.

## 4. Conclusion

The equilibrium sorption isotherm is very important in design of sorption systems. Therefore for finding out the sorption isotherm, the experimental results were analyzed by using Freundlich, Langmuir and DR equations. It is seen that, the linear form of Freundlich and DR equations are in good agreement with the experimental data. The relative adsorption capacity values calculated from Freundlich equation are decreasing with the rise in temperature from 298 K to 318 K for Siral 30. However, a decrease was observed with the increase of tem-

Sample	Temperature (K)	Kc	$\Delta G^{\circ}  (\text{kJ mol}^{-1})$	$\Delta H^{\circ}  (\text{kJ mol}^{-1})$	$\Delta S^{\circ} (\text{kJ mol}^{-1} \text{K}^{-1})$
Pural	298 318	0.046 0.024	7.628 9.860	-25.651	-0.112
Siral 30	298 318	0.042 0.043	7.854 8.319	0.788	-0.024

perature from 298 K to 318 K for Pural sample. The magnitude of sorption energy computed from DR equation is mostly lower than  $8 \text{ kJ mol}^{-1}$ , indicating physical adsorption. Thermodynamic constants were also determined. It is found that adsorption is nonspontaneous nature for all samples. Desorption experiments show that desorption from Pural is possible, whereas desorption from Siral 30 is not possible in 0.1 M HCl and distilled water.

From the standpoint of statistical analysis, it is determined that the type of adsorbent has a positive effect, whereas temperature and pH exhibited a negative effect on the boron adsorption. On the one hand, the interaction between the type of adsorbent and temperature of the solution contributes to boron adsorption from the aqueous solution. On the other hand, the other interactions were not effective on boron adsorption.

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