Adsorption of Boron from Aqueous Solutions by Sepiolite using Full Factorial Design: I. Batch Studies'*

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ABSTRACT: In this study, boron removal from aqueous solution by batch adsorption was investigated and experimental design was applied. Non-activated waste sepiolite (NAWS) and HCl activated waste sepiolite (AWS) were used as adsorbents. An experimental test carried out using 2^3 full factorial design. The results obtained from the study on parameters showed that as pH increased and temperature decreased boron removal by adsorption increased. Adsorbed boron amount on AWS was higher than that of NAWS. Maximum boron removal was obtained at pH 10 and 20°C for both adsorbents. Adsorption data obtained from batch adsorption experiments carried out with NAWS and AWS fitted to the Langmuir equation.

1. INTRODUCTION

There is no easy method for the removal of boron from waters and wastewaters. One or more methods may be applied according to boron concentration *m* medium. For boron removal, main processes that have been studied are (1) precipitation-coagulation, (2) adsorption on oxides, (3) adsorption on active carbon, cellulose or clay minerals, (4) ion exchange with basic exchanger, (5) solvent extraction, (6) membrane filtration, (7) use of boron selective resins (Amberlite XE 243, Amberlite IRA 743) (Öztürk and Kavak, 2003; Okay et al., 1985; Recepoğlu and Beker, 1991; Simonnot et al., 1999; Balkı, 1982; Goldberg et al., 1996).

Over the last few decades adsorption has gained importance as a purification and separation process on an industrial scale. In the adsorption procedures (and for the case of waters and wastewaters), the conventional material used is activated carbon but due to its high cost regeneration is essential.

In this study, waste sepiolite obtained during the production of ornaments and tobacco pipes by carving was preferred as adsorbent. The relatively low cost of sepiolite guarantee its continued • utilisation in the future, and most of the world sepiolite reserves are found in Turkey/Eskişehir (nearly 70%) (Balcı and Dinçel, 2002; Saniz and Nuhoğhı, 1992). Sepiolite is a hydrous magnesium silicate mineral. Its magnesium content provides higher strength while the hydrogen and oxygen provide porosity. In adsorption, adsorbent surface area must be large. Surface area can be increased by activation (Kıpçak, 1999). Several works related to the wastewater treatment using sepiolite have been citted in the literature. Balcı and Dinçel (2002) studied the ammonium removal from solutions using Turkish sepiolite. The high capacity values were also observed for the heavy metal ions removal and wastewater treatment using sepiolite (Garcia Sanchez et al., 1999; Bağ et al., 2000; Brigatti et al., 2000; Sabah et al., 2002).

A technique known as statistical design of experiments is a powerful technique for process

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characterisation, optimisation and modelling. It has been widely accepted in manufacturing industry for improving product performance and reliability, process capability, and yield. It basically involves the process of planning and designing an experiment so that the appropriate data may be collected which then can be analysed and interpreted, resulting in valid and objective conclusions. In a statistically designed experiment, we simultaneously vary the factors involved in an experiment at their respective levels so that a large amount of information can be gained with a minimum number of experimental trials (Antony and Roy, 1999).

Experiments in which the effects of more than one factor on response are investigated are known as full factorial experiments. In a full factorial experiment, both of the (-1) and (+1) levels of every factor are compared with each other and the effects of each of the factor levels on the response are investigated according to the levels of other factors. If number of factors and levels increases, the number of experiments geometrically increases. By factorial planning of the experiments it was possible to investigate the effects of all the variables simultaneously (Yeniay, 2001; Montgomery, 1997; Bayar,2001;).

In this study, boron removal from aqueous solutions by adsorption method was investigated by non activated waste sepiolite (NAWS) and HCl activated waste sepiolite (AWS). Two level factorial design was applied to investigate the effects of the parameters and their interactions on boron removal by batch adsorption. Batch adsorption capacities were calculated.

2. EXPERIMENTAL WORK

2.1. Materials and Methods

NAWS and AWS were used as adsorbents for boron removal from aqueous solution. NAWS was obtained from carving waste, in Eskişehir (Margı) area. NAWS was analysed by XRF in Eskişehir Cement Factory and Magnesia Factory. Chemical analysis results are given in Table 1. NAWS (10g) was activated with 400 mL, 0.75 M HCl in a reactor under reflux condenser at 75°C for 4 h. Adsorbents were dried at 105°C for 2 h and screened before being used. Adsorbent particle sizes used in adsorption experiments were between 71 and 80 um. Surface areas of NAWS and AWS were calculated from Langmuir equation were determined by measurements of the adsorption of N_2 in a NOVA 2200 at 77 K. Surface areas of NAWS and AWS were given in m^2/g: 516.3, 519.06, respectively.

Table 1. Chemical composition of the used NAWS

Constituents	Contents (% w/w)
$Si0_2$	57.51
MgO	27.52
$A1_20_3$	0.09
$Fe20_3$	0.03
CaO	0.9
T1O2	0.01
Na_20	0.02
K_20	0.01
Ignition loss	13.9

The aqueous solution of H3BO3 was prepared by using the analytical grade Merck product. The solution was prepared in such a manner that the initial boron concentration adsorption experiments was held at 600 mg/L. pH was measured with pH meter (Consort P903).

In batch adsorption experiments, known weights of adsorbents (0.5 g) were added to capped volumetric flasks each of which containing 50 ml solution and shaken at 140 rpm in a temperature-controlled water bath (NUVE) with shaker (MEMMERT). Adsorbent and solution mixtures were shaken for 48 h (equilibrium time). After adsorption, samples were centrifuged and boron in supernatants was analysed. Boron was determined using HACH DR-2000 Spectrophotometer by carmine method. All of the tests were duplicated. Different adsorbent doses (100-600 mg) were applied to 50 mL of the solution containing 600 mg/L boron at pH 10 and 20°C in order to find out the effect of adsorbent dosage to boron removal. Langmuir and Freundlich isotherms were employed to study the adsorption capacity of the adsorbent.

2.2. Statistical Design of Experiments

The statistical optimization technique using full factorial design of experiments is generally applied to determine the boundary conditions, which allows the maximum output of the desired products. Using a proper design matrix one can obtain a regression equation, which highlights the effect of individual parameters and their relative importance in given operation/process. The interactional effects of two or more variables can also be known, this is not possible in a classical experiment (Sing et al., 2002).

The principal steps of statistically designed experiments are: determination of response variables, factors and factor levels; choice of the experimental design; and statistical analysis of the data. Today, the most widely used experimental design to estimate main effects, as well as interaction effects, is the 2" factorial design, where each variable is investigated at two levels. Research can be designed for multiple factors and treatments, but data analysis and treatment establishment becomes more complex and time consuming as the number of factors and treatments increase (Montgomery, 1997). So, 2^3 factorial design was selected in this study. In this investigation for quantification of the effects of the three variables on the boron removal, a two level factorial design of experiments was adopted. The variables studied are adsorbent type (NAWS.AWS), pH of solution (5.75,10) and temperature (20,40°C). The number of experiments required for understanding all the effects is given by $a^k=2^3=8$, where a is the number of levels and k is the number of factors. The two levels assigned to each variable are expressed in coded form as +1 and -1 (Kar et al., 2000). The regression equation developed from different sets of experiments show the dependence of yield on individual parameters as well as interactions for simultaneous variations of parameters. So the final aim of the statistical design of experiments is to obtain a statistically sound regression model.

3. RESULTS AND DISCUSSION

3.1. Statistical Analysis

In order to examine the main factors and their interactions for the boron removal by adsorption, a factorial of the type 2^3 has been used. The experimental design involved 3 variables at 2 levels (i.e. high and low). In this case the total number of experiments becomes 8, but totally 16 experiments were performed because each experiment was done two times. The variables and levels for the study are given in Table 2. The first level variable was designated as (-1) and the second level as (+1). These levels are selected arbitrarily. In table 2, ^ ,Xj and ^represent the levels of adsorbent type, pH of solution and temperature, respectively, and X,, X_2 and $X_3$are the corresponding values in coded forms. The experimental matrix along with actual and coded scales are present is shown in Table 3.

The regression equation for the matrix is represented by the following expression (Singh et al., 2002):

$$Y_t = b_0 + b_1X_{1i} + b_2X_{2i} + b_3X_{3i} + b_{12}X_{1i}X_{2i} + b_{13}X_{1i}X_{3i} + b_{23}X_{2i}X_{3i} + b_{123}X_{1i}X_{2i}X_{3i} \tag{1}$$

The main and interaction coefficients have been calculated by following relations(Singh et al., 2002):

$$b_o = \sum \frac{Y_t}{N} \tag{2}$$

Table 2. Actual and vis a vis coded values of parameters in 2^3 full factorial design for boron removal by adsorption

Level of Variables	Adsorbent type		pH of solution		Temperature (°C)	
	Actual (x_1)	Coded (X_1)	Actual (x_2)	Coded (X_2)	Actual (x_3)	Coded (X_3)
First level	AWS	-	Initial(5.75)	-	20	-
Second level	NAWS	+	Adjusted (10)	+	40	+

Table 3. Experimental matrix

Serial Number <i)	Adsorbent type		pH of solution		Temperature (°C)		Response $(Y,)$	
	Actual	Coded $X,,$	Actual	Coded $X_2,$	Actual	Coded Xj,		
1	**AWS**	**-**	**5.75**		20	**-**	$Y,$	$Y,$
2	**NAWS**	+	**5.75**		20	**-**	Y_2	Y_m
3	**AWS**	**-**	**10**	**+**	20	**-**	$Y,$	**r,,**
4	**NAWS**	+	**10**	**+**	20	**-**	Y_4	Yñ
5	**AWS**	**-**	**5.75**		40	+	Y_s	Y_{13}
6	**NAWS**	+	**5.75**		40	+	Y_s	**Y,4**
7	**AWS**	**-**	**10**	**+**	40	+	Y_7	Yu
S	**NAWS**	+	**10**	**+**	40	+	Y»	YM

$$b_j = \sum \frac{X_{ji} Y_i}{N} \qquad (3)$$

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

where $Y,$ is the response (adsorbed boron amount); and X_{Jt}values $(j = 1,2,3;\ i = 1,2,3\ldots\ldots,16)$represent the corresponding parameters in their coded forms (Table 3); b_0 gives the average value of the results obtained for the adsorbed boron amount; fe,, b_2 and é$_3$ are the linear coefficients (independent parameters); b_n, b_n, b^ and b_{123} are the interaction coefficients and N is the number of total experiments. Coefficients b_{lt} b_2 and 6$_3$show, respectively, the effect of adsorbent type, pH of solution and temperature. Coefficients b_n, b_n, and b_n show the interacting effects of two variables at a time and b_m shows the interacting effect of all three variables taken at a time. The values of regression coefficients determined are given in Table 4. The design matrix and the results showing adsorbent boron amount are shown in Table 5. The results obtained from the trial runs are incorporated in the regression Eq. (1) and thus, the equation for boron removal by adsorption becomes

$$Y=0.315-0.015X,+0.09X_2-0.2125X3+0.035XiX_2 \\ +0.0375XiX3-0.0575X_2X3-O.OI75X_1X_2X_3 \qquad (5)$$

The effect of individual variables and interactional effects can be estimated from the above equation. According to this equation, pH of solution have a positive effect, while adsorbent type and temperature has a negative effect, on the boron removal by adsorption in the range of variation of each variable selected for the present study. On the other hand, temperature has the greatest effect on boron removal, which is followed by pH and pH-temperature interaction respectively. A negative value for the effect indicates that the measured value (adsorbed boron amount) decreased as the factor was changed from its first level to its second level (Kim et al., 2002).

Table 4. Values of model coefficients

Main and interaction coefficients	Values
*.	0.3150
$b,$	-0.0150
b_2	0.0900
b_3	-0.2125
b_{12}	0.0350
b_{13}	0.0375
bv	-0.0575
bm	-0.0175

Variance of every factor and the sequence of importance of the factors determined by the F-test (Hsher test) method (Barrado et al., 1996; Morais et al., 1999). Using Fisher's test, not only effects and interactions without meaning can be eliminated, but the ones that have more influence on the boron removal by adsorption process can also be verified. The regression equation was tested to see how it fitted with the observations, using Fisher's adequacy test at the 90%, 95%, 99% confidence levels (probability levels: a= 0.1; a=0.05; a=0.01, respectively). According to analysis of variance, calculated F ratios and decisions are given in Table 6. Comparing the calculated F values with Fisher's F values, it seems that in all cases calculated F is greater than Fisher's F values [F<u(1,8)]: 3.46; [Foo5(1,8)] : 5.32; [F_0.oi(1,8)]: 11.26. So, all the variables and interactions are found to be effective on boron removal by adsorption.

Table 5. Design of trial runs (in coded form) for boron removal by adsorption in two replicate experiments

Trial No	„	x_2	x_3	*X1X2*	*X1X3*	x_2x_3	*XIX2X3*	***Y*** **adsorbed1 boron amount (g/L)**	***Y*** **adsorbed boron amount (g/L)**	***Y*** **average adsorbed boron amount (g/L)**
1		-	-	+	+	+	-	**0.40**	**0.42**	**0.41**
2	+	-	-	-		+	+	**0.20**	**0.20**	**0.20**
3		+	-		+	-	+	**0.60**	**0.60**	**0.60**
4	+	+	-	+		-	-	**0.60**	**0.60**	**0.60**
5		-	+	+		-	+	**0.11**	**0.17**	**0.14**
6	+	-	+		+	-	-	**0.15**	**0.15**	**0.15**
7		+	+	-		+	-	**0.17**	**0.17**	**0.17**
8	+	+	+	+	+	+	+	**0.25**	**0.25**	**0.25**

Table 6. According Ito analysis of variance F ratios and decisions

Soiree of variation	**F ratio**	**Decision o=0.1**	**Decision a=0.05**	**Decision a=0.01**
X,	**14.40**	**Effective**	**Effective**	**Effective**
x_2	**518.40**	**Effective**	**Effective**	**Effective**
x_3	**1210**	**Effective**	**Effective**	**Effective**
x,x_2	**78.40**	**Effective**	**Effective**	**Effective**
X1X3	**90**	**Effective**	**Effective**	**Effective**
X2X3	**211.60**	**Effective**	**Effective**	**Effective**
A/A2A3	**19.60**	**Effective**	**Effective**	**Effective**

According to the F values the most important parameter affecting the boron removal by adsorption is temperature, which is followed by pH of solution. The adsorbent type has the least effect. The interaction between pH of solution and temperature was an important significant factor for boron removal by adsorption. Fischer's test at 0.1, 0.05 and 0.01 probability levels indicated that the model is adequate. Then it can be concluded that the statistical analysis confirmed that the adsorption was favored by an increase in pH and unfavored by an increase in temperature and AWS was more effective than the NAWS for boron adsorption.

3.2. Effect of Adsorbent Dosage

Figure 1 gives the removal percentage of boron as a function of adsorbent dosage. In general, the increase in adsorbent dosage increased the percent removal of boron, which is due to the increase in adsorbent surface area. The results obtained in the study are in agreement with this. Adsorbent dosage was varied from 2 to 12 g/L. It is evident that boron removal by adsorption is better in the case of using AWS. The results also clearly indicate that the removal efficiency increases up to optimum dosage beyond which the remoyal efficiency is negligible.

3.3. Adsorption isotherms

Several models have been published in the literature to describe experimental data of adsorption isotherms. The Langmuir and Freundlich models are the most frequently employed models (Banat et al., 2000). In this work, both models were used to describe the relationship between the adsorbed amount of boron and its equilibrium concentration in solution,

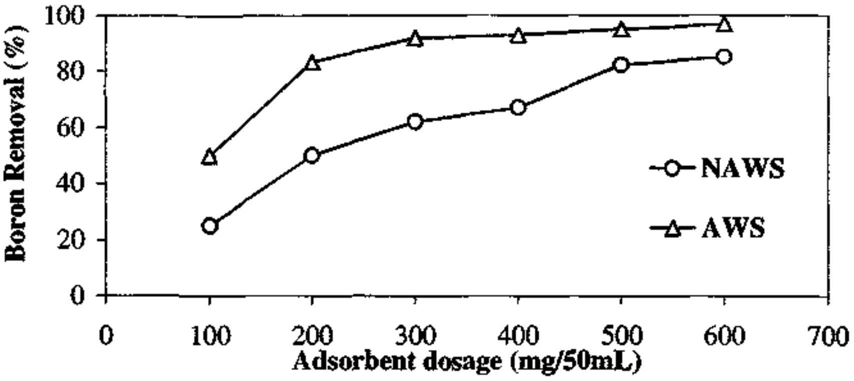

Figure 1. Effect of adsorbents dosage on the removal of boron by adsorption (at pH 10 and 20°C).

Langmuir isotherm is represented by the following equation (Namasivayam and Kavitha, 2002):

$$\frac{C_e}{q_e} = \frac{1}{q_o b} + \frac{C_e}{q_o} \qquad (6)$$

where C_e is the concentration of the boron solution (mg/L) at equilibrium and ^.is the amount adsorbed at equilibrium (mg/g).

The constant q_0 signifies the adsorption capacity (mg/g) and b is related to the energy of adsorption (L/mg). The linear plot of Cjq_e versus C_e shows that adsorption follows a Langmuir isotherm (Rg.2). Values of q_B and b were calculated from the slope and intercept of the linear plots and are presented in Table 7. The applicability of the Langmuir isotherm suggests the monolayer coverage of the boron adsorption onto sepiolites (Namasivayam and Kavitha, 2002).

To determine if the boron adsorption process by NAWS and AWS is favourable or unfavourable for the Langmuir type adsorption process, the isotherm shape can be classified by a term "RL", a dimensionless constant separation factor, which is defined below (Namasivayam and Kavitha, 2002):

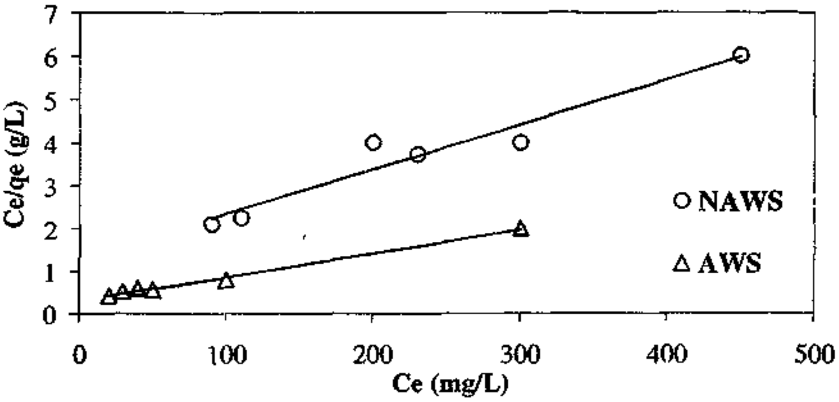

Figure 2. Langmuir plots for boron removal by adsorption (at pH 10 and 20°C).

$R_L=1/(1+K7_a)$ (7)

where RL is a dimensionless separation factor, C_0 is the initial boron concentration (mg/L) and *b* is Langmuir constant (L/mg). The parameter RL indicates the shape of the isotherm accordingly:

RL>1	Unfavourable
$R_L=1$	Linear
0<RL<1	Favourable
$R_L=0$	Irreversible

Both of the calculated R_L values (Table 7) indicated that adsorption of boron on NAWS and AWS are favourable at 600 mg/L initial boron concentration, 20°C and pH 10.

The Freundlich isotherm was also applied for the boron removal by adsorption. Freundlich isotherm model is given by the following equation (Namasivayam and Kavitha., 2002):

log^log/^+Cl/MlogC, (8)

where K_f and n are Freundlich adsorption isotherm constants, being indicative of the adsorption capacity and intensity of adsorption. Values of K_f and n were calculated from the intercept and slope of the plots of $log q_e$ versus $logC_e$ (Fig. 3). In general, as the K_f value increases, the adsorption capacity of the adsorbent increases. The isotherm data are given in Table 7. According to K_f value and q_0 value, AWS is more effective than NAWS. It has been shown using mathematical calculations that n was between 1 and 10 representing beneficial adsorption (Sivaraj et al., 2001). So both of the adsorbents used in the study provide beneficial adsorption.

Table 7. Langmuir and Freundlich constants

Adsorbent	Langmuir constants				Freundlich constants		
	q_0 (mg/g)	b (L/mg)	R_L	R^2	K_f	n	R^2
NAWS	96.15	0.008	0.172	0.939	8.34	2.74	0.865
AWS	178.57	0.0182	0.084	0.994	14.13	2.28	0.914

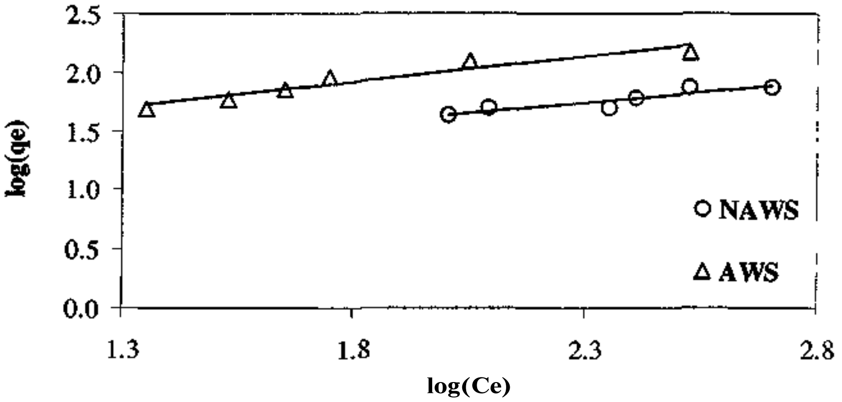

Figure 3. Freundlich plots for boron removal by adsorption (at pH 10 and 20°C).

4. CONCLUSIONS

From the statistical analysis it was found out that the pH has a positive effect, while temperature has a negative effect on the boron removal by adsorption. On the other hand, interaction between pH and temperature was a significant factor in boron removal. Other interactional parameters and adsorbent activation also contribute to the increase in adsorbed boron amount, though the effect is rather small. Maximum boron removal was obtained at 20°C and pH 10 for both adsorbents. The adsorption was found to be exothermic in nature. The Langmuir isotherm is obeyed better than the Freundlich isotherm, as is evident from the values of regression coefficients.

The batch adsorption capacities were found in mg/g 96.15 and 178.57 for NAWS and AWS, respectively.

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