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Boron Removal from Aqueous Solutions by Adsorption on Waste Sepiolite and Activated Waste Sepiolite Using Full Factorial Design

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Abstract. In the present paper, boron removal from aqueous solution by adsorption was investigated and 2^3 full factorial design was applied. Non activated waste sepiolite (NAWS) and HCl activated waste sepiolite (AWS) were used as adsorbents. Regression equation formulated for boron adsorption was represented as a function of response variables. 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. The batch adsorption capacities were found in mg/g: 96.15 and 178.57 for NAWS and AWS, respectively. The capacity value for column study was obtained by graphical integration as 219.01 mg/g for AWS. The Thomas and the Yoon-Nelson models were applied to experimental data to predict the breakthrough curves and to determine the characteristic parameters of the column useful for process design.

Keywords: boron removal, adsorption, waste sepiolite, experimental design, packed bed column

1. Introduction

Boron, the fifth element in the periodic table, is the only electron-deficient non-metallic element. It has a great affinity for oxygen. Boron minerals occurring in nature in more than 200 compounds are known variously as tincal, colemanite, ulexite, and kernite, depending on the ratios of calcium, sodium, magnesium, etc., and water content present in the mineral (Bayar, 2001; Şahin, 2002).

Boron and boron compounds are widely used in industrial applications (Morales et al., 2000; Badruk et al., 1999a; Sarıiz and Nuhoğlu, 1992). During the production of boron compounds, many of these are introduced into the environment in the form of waste. Boncukcuoğlu et al. (2002) showed that the wastes such as borax slime, tincal waste, concentration wastes and thromel sieve waste (TSW) contain impurities that accelerate the normal setting and hardening of building materials produced from them. In that study, Portland cement was prepared by adding TSW to clinker. The authors investigated the effects of TSW on the mechanical properties of the prepared Portland cement and suggested that TSW can be used as an additive to cement up to 25% by weight.

Boric acid and boron salts have extensive industrial use in the manufacture of glass and porcelain, in wire drawing, the production of leather, carpets, cosmetics and photographic chemicals, for fireproofing fabrics, and weatherproofing wood. Boron compounds are used in certain fertilisers for the treatment of boron deficient soils. Boric acid, which has mild bactericidal and fungicidal properties, is used as disinfectant and as food preservative. Borax is widely used in welding and brazing of metals, and more recently, boron

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compounds have found applications for hand cleansing, high-energy fuels, cutting fluids and catalysts (Şahin, 2002).

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 (Okay et al., 1985). Turkey is the first in production with 1.2 million tons of boron minerals. At Kırka (Eskişehir) boron plant, 550,000 tons/year concentrated tincal, 160,000 tons/year borax pentahydrate, 60,000 tons/year anhydrous borax and 17,000 tons/year borax decahydrate were produced. Boron plants may cause some environmental problems. Wastewater from boron plants is discharged to ponds. Wastewater ponds occupy a wider area than the boron plant area. Wastewater having high boron content may damage agricultural areas in the case of overflow from wastewater ponds. For this reason boron must be removed from wastewater (Öztürk et al., 2002).

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 in 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).

A very low boron content is required in irrigation water for certain metabolic activities, but if its concentration is only slightly higher, plant growth will exhibit effects of boron poisoning, which are yellowish spots on the leaves and fruits, accelerated decay and ultimately plant expiration (Nadav, 1999; Bayar, 2001; Badruk et al., 1999b; Hatcher and Bower, 1958). Referring to Nable et al. (1997), safe concentrations of boron in irrigation water are 0.3 mg/L for sensitive plants, 1–2 mg/L for semi tolerant plants, and 2–4 mg/L for tolerant plants. Adsorption is a separation process in which certain components of a fluid phase are transferred to the surface of a solid adsorbent. 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 (Kopaç and Kocabaş, 2002; Morais et al., 1999). Different adsorbents can be used for adsorption. For example, boron removal from aqueous solutions by adsorption using alumina and powdered activated carbon was investigated by applying an experimental design by Öztürk and Kavak (2003). It has been reported that the batch adsorption capacities of alumina and powdered activated carbon are 86.21, 166.67 mg/g, respectively. The amount of adsorbed boron also depends on the distribution of $B(OH)_3$ and $B(OH)_4^-$ which are controlled by pH. The three species $B(OH)_3$, $B(OH)_4^-$, and OH^- compete for the active sites on the surface. The amount of adsorbed boron is determined by the product of the activities of $B(OH)_3$, $B(OH)_4^-$ and OH^- and their affinity coefficients. The concentrations of $B(OH)_4^-$ and OH^- are low, and $B(OH)_3$ is the major component in low pH solution. The amount of adsorbed boron is lower at low pH due to the low affinity coefficient of $B(OH)_3$, which is much lower than that of $B(OH)_4^-$. The degree of boron removal by adsorption increased by increasing $B(OH)_4^-$ concentration, which increases with pH (Yingkai and Lan, 2001; Şahin, 2002).

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; Sarıiz and Nuhoğlu, 1992). Sepiolite is a hydrous magnesium silicate mineral. Its magnesium content provides higher strength while the hydrogen and oxygen provide porosity. In liquid phase, sepiolite adsorbs especially molecules with basic character selectively and effectively. In adsorption, adsorbent surface area must be large. Surface area can be increased by activation (Kıpçak, 1999; Radojevic et al., 2002). During acid activation, the proton (H^+) of the acids replaces part of the Mg^{2+} ions located in the octahedral sheet. Furthermore, more carbonates in sepiolite are partially decomposed leading to new pores and fresh surfaces (Kara et al., 2003). 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. They showed that the maximum adsorbed amount was 3.50 mmol NH_4^+/g. 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; Figueiredo et al., 2000; Sabah et al., 2002).

Ramirez et al. (1995) studied with different water/(lime and sand) ratios and found the optimum amount of sepiolite which could be added to the mortar for achieving the best plasticity.

A technique known as statistical design of experiments is a powerful technique for process 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 (Rocak et al., 2002; Antony and Roy, 1999; Şayan and Bayramoğlu, 2000; Annadurai et al., 2002).

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 (Bayar, 2001; Montgomery, 1997; Yeniay, 2001).

In this study, boron removal from aqueous solutions by batch and column adsorption methods 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. The Thomas and Yoon-Nelson models were applied to experimental data obtained from column study. Batch and column capacities were calculated.

2. Experimental

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 (10 g) 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 μm. 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)
SiO_2	57.51
MgO	27.52
Al_2O_3	0.09
Fe_2O_3	0.03
CaO	0.90
TiO_2	0.01
Na_2O	0.02
K_2O	0.01
Ignition loss	13.90

2.2. Batch Adsorption Studies

The aqueous solution of H_3BO_3 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. The effect of pH was studied by adjusting the pH of boron solutions using dilute HCl and NaOH solutions with two adsorbents at 20°C. The effect of temperature was carried out by AWS at 20, 30, 40 and 60°C in the temperature-controlled water bath with shaker. Boron plant wastewaters can contain various ions such as sulphate, sodium, calcium, magnesium, etc. The effects of Na_2SO_4 and $CaCl_2$ at various concentrations on boron removal by adsorption using AWS was studied.

2.3. *Column Studies*

A glass column (0.7 cm ID and 15 cm length) was filled with 0.5 g of AWS on glass wool support. Boron solution (600 mg/L B) at 20°C and pH 10 was delivered downflow to the column using a peristaltic pump (ATTO SJ 1211 model) at a 0.15 mL/min flow rate. To obtain breakthrough curve the effluent was collected as 1.5 cm^3 fractions with a fraction collector (Spectra/chrom CF-1) and analysed. Column studies were terminated when the column reached exhaustion. The desorption studies carried out after the column adsorption studies were conducted at 20°C and 0.15 ml/min flow rate. The adsorbed boron was desorbed from AWS by using 2 M H_2SO_4 solution.

2.4. *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^n 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 (Chegrouche and Bensmaili, 2002; Al-Asheh et al., 2002; Kar et al., 2000; Mishra et al., 2000; Ragonese et al., 2000; Massumi et al., 2002). 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, x_1, x_2 and x_3 represent the levels of adsorbent type, pH and temperature, respectively, and X_1, X_2 and X_3 are the corresponding values in coded forms. The experimental matrix along with natural 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):

$$Y_i = b_o + b_1 X_{1i} + b_2 X_{2i} + b_3 X_{3i} + b_{12} X_{1i} X_{2i} + b_{13} X_{1i} X_{3i} + b_{23} X_{2i} X_{3i} + b_{123} X_{1i} X_{2i} X_{3i} \quad (1)$$

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

	Adsorbent type		pH of solution		Temperature (°C)	
Level of variables	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.

	Adsorbent type		pH of solution		Temperature (°C)		Response (Y_i)	
Serial number (i)	Actual	Coded X_{1i}	Actual	Coded X_{2i}	Actual	Coded X_{3i}		
1	AWS	−	5.75	−	20	−	Y_1	Y_9
2	NAWS	+	5.75	−	20	−	Y_2	Y_{10}
3	AWS	−	10	+	20	−	Y_3	Y_{11}
4	NAWS	+	10	+	20	−	Y_4	Y_{12}
5	AWS	−	5.75	−	40	+	Y_5	Y_{13}
6	NAWS	+	5.75	−	40	+	Y_6	Y_{14}
7	AWS	−	10	+	40	+	Y_7	Y_{15}
8	NAWS	+	10	+	40	+	Y_8	Y_{16}

The main and interaction coefficients have been calculated by following relations (Sahoo et al., 2001):

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

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

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

where Y_i is the response (adsorbed boron amount); and X_{ji} values ($j = 1, 2, 3; i = 1, 2, 3, \ldots, 16$) represent the corresponding parameters in their coded forms (Table 3); b_o gives the average value of the results obtained for the adsorbed boron amount; b_1, b_2 and b_3 are the linear coefficients (independent parameters); b_{12}, b_{13}, b_{23} and b_{123} are the interaction coefficients and N is the number of total experiments. Coefficients b_1, b_2 and b_3 show, respectively, the effect of adsorbent type, pH and temperature. Coefficients b_{12}, b_{13}, and b_{23} show the interacting effects of two variables at a time and b_{123} 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)

Table 4. Values of model coefficients.

Main and interaction coefficients	Values
b_0	0.3150
b_1	−0.0150
b_2	0.0900
b_3	−0.2125
b_{12}	0.0350
b_{13}	0.0375
b_{23}	−0.0575
b_{123}	−0.0175

and thus, the equation for boron removal by adsorption becomes

$$\begin{aligned} Y = {} & 0.315 - 0.015X_1 + 0.09X_2 - 0.2125X_3 \\ & + 0.035X_1X_2 + 0.0375X_1X_3 - 0.0575X_2X_3 \\ & - 0.0175X_1X_2X_3 \end{aligned} \tag{5}$$

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

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

Trial no.	X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	$X_1X_2X_3$	Y adsorbed 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

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).

Variance of every factor and the sequence of importance of the factors determined by the F-test (Fisher test) method (Barrado et al., 1996; Furlanetto et al., 2000; Hung et al., 2002; Esteves de Silva et al., 2001; 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: $\alpha = 0.1$; $\alpha = 0.05$; $\alpha = 0.01$, 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 [$F_{0.1}$(1,8)]: 3.46; [$F_{0.05}$(1,8)]: 5.32; [$F_{0.01}$(1,8)]: 11.26. So, all the variables and interactions are found to be effective on boron removal by adsorption.

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.

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

Source of variation	F ratio	Decision $\alpha = 0.1$	Decision $\alpha = 0.05$	Decision $\alpha = 0.01$
X_1	14	Effective	Effective	Effective
X_2	518	Effective	Effective	Effective
X_3	1210	Effective	Effective	Effective
X_1X_2	78	Effective	Effective	Effective
X_1X_3	90	Effective	Effective	Effective
X_2X_3	212	Effective	Effective	Effective
$X_1X_2X_3$	20	Effective	Effective	Effective

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 removal efficiency is negligible.

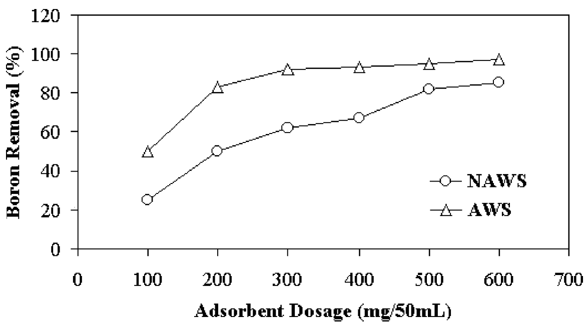

Figure 1. Effect of adsorbents dosage on the removal of boron by adsorption (at pH 10 and 20°C).

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.

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

$$\frac{C_e}{q_e} = \frac{1}{q_o b} + \frac{C_e}{q_o} \tag{6}$$

where C_e is the concentration of the boron solution (mg/L) at equilibrium and q_e is the amount adsorbed at equilibrium (mg/g). The constant q_o signifies the adsorption capacity (mg/g) and b is related to the energy of adsorption (L/mg). The linear plot of C_e/q_e versus C_e shows that adsorption follows a Langmuir isotherm (Fig. 2). Values of q_o 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 (Demirbaş et al., 2002; Namasivayam et al., 2001).

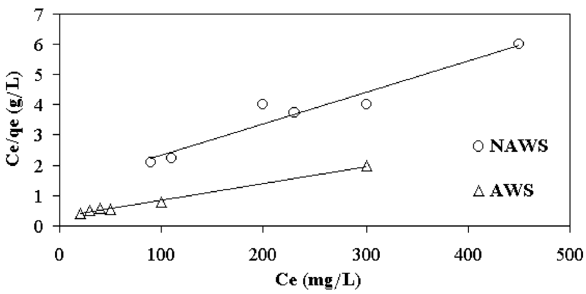

Figure 2. Langmuir plots for boron removal by adsorption (at pH 10 and 20°C).

Table 7. Langmuir and Freundlich constants.

	Langmuir constants				Freundlich constants		
Adsorbent	q_o (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	0.018	0.084	0.994	14.13	2.28	0.914

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 "R_L", a dimensionless constant separation factor, which is defined below (Altındoğan et al., 2000; Rao et al., 2002):

$$R_L = 1/(1 + bC_o) \tag{7}$$

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

$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	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):

$$\log q_e = \log K_f + (1/n) \log C_e \tag{8}$$

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 $\log C_e$ (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_o value, AWS is more effective

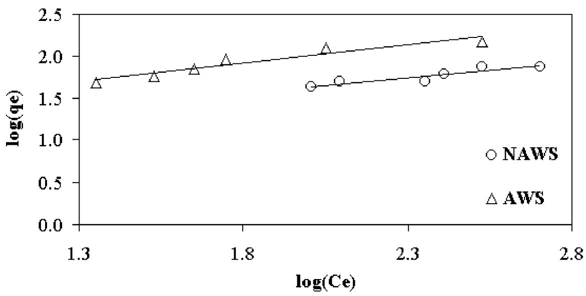

Figure 3. Freundlich plots for boron removal by adsorption (at pH 10 and 20°C).

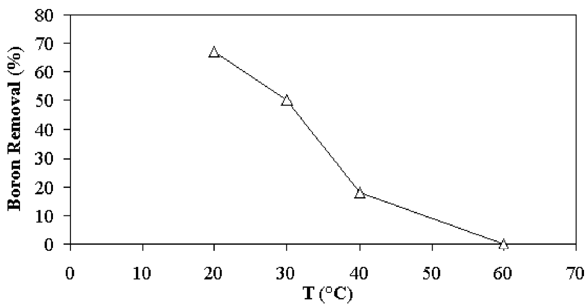

Figure 5. Effect of temperature on the boron removal by adsorption using AWS (at pH 5.75).

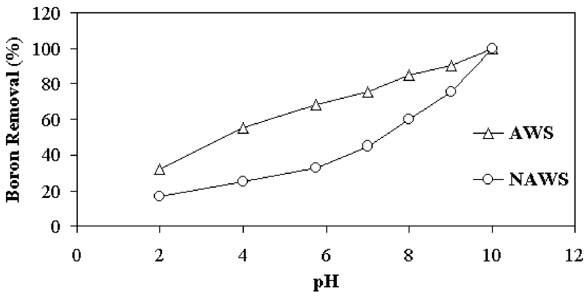

Figure 4. Effect of pH on the boron removal by adsorption at 20°C.

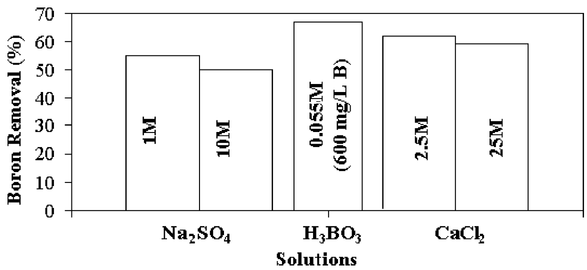

Figure 6. Effect of added salts concentration on the boron removal percent for AWS (at pH 5.75).

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.

3.4. *Effect of pH*

The adsorption of boron was studied over the pH range 2–10 (Fig. 4). The maximum uptake of boron takes place at pH 10 for both adsorbents.

3.5. *Effect of Temperature*

The effect of temperature on the adsorption of boron on AWS is shown in Fig. 5. The uptake of boron was found to decrease with increasing temperature, indicating that boron adsorption on the adsorbent surface was favoured at lower temperatures. The boron removal percent followed the order 20°C > 30°C > 40°C > 60°C. The decrease in adsorption with increasing temperature indicated exothermic nature of the adsorption process.

3.6. *Effects of Other Ions*

In the present study all of the tests were done with H_3BO_3 solution. However in real boron plant wastewaters contain various species. The effect of presence of two salts, i.e. Na_2SO_4 and $CaCl_2$ on boron adsorption was studied as a function of concentration (Fig. 6). Tests were conducted in the presence of (1 and 10 M) Na_2SO_4 and (2.5 and 25 M) $CaCl_2$ solutions. It was observed that the decrease in the adsorption is about 6–18%.

3.7. *Column Studies*

The performance of packed beds is described through the concept of the breakthrough curve. The breakthrough curve shows the loading behaviour of boron to be removed from solution in a fixed bed and is usually expressed in terms of adsorbed boron concentration (C_{ad} = inlet boron concentration (C_o) − outlet boron concentration (C_e)) or normalised concentration defined as the ratio of effluent boron concentration to inlet boron concentration (C_e/C_o) as a function of time or volume of effluent for a given bed height (Aksu and Gönen, 2004). The area under the breakthrough curve obtained by integrating the adsorbed concentration (C_{ad}; mg/L) versus the throughput volume (V; L) plot can be used to find the total adsorbed boron quantity (maximum column capacity). Total adsorbed boron quantity (q_o; mg/g) in the column for a given feed concentration and flow rate is calculated from Eq. (9)

$$q_o = \int_o^{V_T} \frac{(C_o - C_e)dV}{m} \tag{9}$$

where V_T is the volume of effluent collected upon exhaustion of the bed and m is the mass of the adsorbent (g). The capacity value q_o was obtained by graphical integration as 219.01 mg/g. The height of the mass transfer zone h_z is given by the relation (Agyei et al., 2002):

$$h_z = h_T[(V_z/V_i - 0.5V_z)] \tag{10}$$

$$V_z = V_T - V_E \tag{11}$$

where h_T is the bed height and V_E is the volume of effluent collected up to breakthrough. The value of h_z was calculated as 0.53 cm for boron removal by AWS at studied column.

3.7.1. Application of The Thomas Model. Successful design of a column adsorption process requires prediction of the concentration-time profile or breakthrough curve for the effluent. The maximum adsorption capacity of an adsorbent is also needed in design. Traditionally, The Thomas model is used to fulfil the purpose. The model has the following form (Mathialagan and Viraragravan, 2002).

$$\frac{C_e}{C_o} = \frac{1}{1 + \exp\left[\frac{K_T(q_o m - C_o V)}{\theta}\right]} \tag{12}$$

where K_T is the Thomas rate constant (L/min·mg) and θ is the volumetric flow rate (L/min). The linearized form of the Thomas model is as follows:

$$\ln\left(\frac{C_o}{C_e} - 1\right) = \frac{K_T q_o m}{\theta} - \frac{K_T C_o}{\theta} V \tag{13}$$

The kinetic coefficient K_T and the adsorption capacity of the bed q_o can be determined from a plot of $\ln[(C_o/C_e) - 1]$ against t at a given flow rate.

The Thomas equation coefficients for boron adsorption by AWS were $K_T = 2.5\ 10^{-5}$ L/min·mg and $q_o = 219.53$ mg/g. The value of q_o is a measure of the adsorption capacity at the AWS for boron. The theoretical predictions based on the model parameters are compared in Fig. 7 with the observed data.

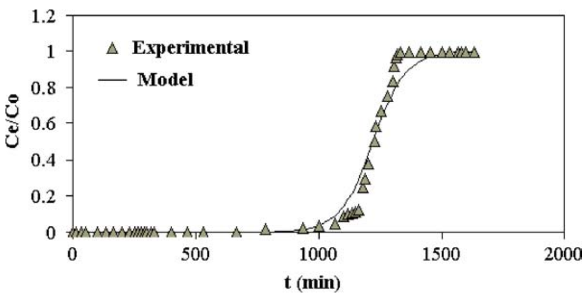

Figure 7. Comparison of the experimental and predicted breakthrough curves for AWS according to Thomas model (at 20°C, pH 10 and C_o 600 mg/L).

3.7.2. Application of the Yoon and Nelson Model. This model is based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent. The Yoon and Nelson model not only is less complicated than other models, but also requires no detailed data concerning the characteristics of adsorbate, the type of adsorbent, and the physical properties of adsorption bed.

The Yoon and Nelson equation regarding to a single component system is expressed as Aksu and Gönen (2004):

$$\frac{C_e}{C_o} = \frac{1}{1 + \exp[k(\tau - t)]} \tag{14}$$

where k is the rate constant (L/min); τ, the time required for 50% adsorbate breakthrough (min) and t is the breakthrough (sampling) time (min). The linearized form of the Yoon and Nelson Model is as follows:

$$\ln \frac{C_e}{C_o - C_e} = kt - \tau k \tag{15}$$

The calculation of theoretical breakthrough curves for a single-component system requires the determination of the parameters k and τ for the adsorbate of interest. These values may be determined from available experimental data. The approach involves a plot of $\ln[C_e/(C_o - C_e)]$ versus sampling time (t) according to Eq. (15). The model parameters for boron adsorption by AWS were $k = 0.019$ 1/min and $\tau = 1197.5$ min.

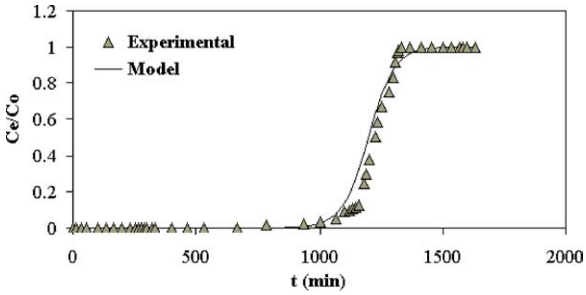

Figure 8. Comparison of the experimental and predicted breakthrough curves for AWS according to Yoon-Nelson model (at 20°C, pH 10 and C_o 600 mg/L).

Alternatively, τ can also be obtained at the adsorption time when $\ln[C_e/(C_o - C_e)]$ is zero because of the fact that by definition τ is the adsorption time when C_e is the one-half of C_o.

These values were used to calculate the breakthrough curve. The theoretical curves were compared with the corresponding experimental data in Fig. 8. The experimental breakthrough curves were very close to those predicted by the Thomas and the Yoon-Nelson Model.

The derivation for Eq. (14) was based on the definition that 50% breakthrough of the adsorption process occurs at τ. Accordingly, the bed should be completely saturated at 2τ. Due to the symmetrical nature of breakthrough curve, the amount of boron adsorbed by the AWS is one half of the total boron entering the adsorption column within the 2τ period. Hence the following equation can be written (Lin and Wang, 2002).

$$q_o = \frac{1}{2}C_o\theta(2\tau) = C_o\theta\tau \qquad (16)$$

The above equation establishes the relation among the adsorption capacity of the column (q_o), inlet concentration (C_o), liquid flow rate (θ) and the 50% breakthrough time (τ). q_o was calculated as 215.55 mg/g using Yoon and Nelson model.

3.8. Desorption Studies

Figure 9 shows the desorption behaviour of boron. Desorption tests performed with 2 M H_2SO_4 gave 2.46% desorption value. Because the sepiolite samples used in this study is a waste material and boron desorption value is very low (only 2.46%), the regeneration of adsorbent was not investigated. The addition of the boron adsorbed adsorbent into clinker or mortar may be investigated in another study.

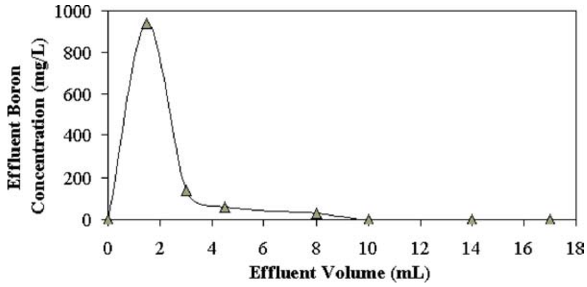

Figure 9. Desorption of boron.

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. The column capacity value was obtained by graphical integration as 219.01 mg/g for AWS. The Thomas and the Yoon-Nelson models were applied to data obtained from experimental studies performed on fixed column to predict the breakthrough curves and to determine the column kinetic parameters. The capacity values were obtained as 219.53 mg/g and 215.55 mg/g using the Thomas and the Yoon-Nelson models, respectively, for AWS.

Nomenclature

b	Parameter of the Langmuir equation (L/mg)
b_o	Average adsorbed boron amount (g/L)
b_1, b_2, b_3	Linear coefficients
b_{12}, b_{13}, b_{123}	Interaction coefficients
C_{ad}	Adsorbed boron concentration in the column (mg/L)
C_o	Initial boron concentration (mg/L)
C_e	Concentration of boron at equilibrium (mg/L)

F	The value of Fisher table
h_T	Bed height (cm)
h_z	Height of the mass transfer zone (cm)
k	Kinetic constant in the Yoon and Nelson model (L/min)
K_f	Parameter of the Freundlich equation ((mg/g)(L/mg)$^{1/n}$)
K_T	Kinetic constant in the Thomas model (L/mg·min)
m	Adsorbent amount (g)
n	Freundlich adsorption constant
N	The number of total experiments
q_e	Amount of boron adsorbed at equilibrium (mg/g)
q_o	Monolayer capacity of the adsorbent (mg/g)
R_L	Dimensionless separation factor
t	Time (min)
V	Throughput volume (L)
V_E	Volume of effluent collected up to breakthrough (L)
V_T	Volume of effluent collected upon exhaustion of the bed (L)
Y_i	Performance value of ith experiment
X_{ji}	Corresponding parameter in coded forms

Greek Letters

α	Probability level
θ	Volumetric flow rate (1/min)
τ	Time required for 50% adsorbate breakthrough (min)

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