

A Mathematical Model for Explanation of Ion Exchange of the Boric Acid Adsorption

SAMI SAHIN

*Department of Chemistry, Istanbul Technical University,
Maslak 80626 Istanbul, Turkey*

(Received 11th May, 1996, revised 19th May, 1997)

Summary: Present study offers a mathematical model to investigate ion exchange process in removal of boron columnar operation systems from wastes of an Boric Acid producing plant.

Bed depth service time and logit methodologies are very effective in examining ion exchange process for removing boron by columnar operation. They are employed in this paper for the development of a convenient mathematical model. Such a model provides opportunity for the assessment in process parameters among which are the bed depth, ion exchange rate, influent concentration as well as the pH effect on the service time. Experimentally obtained data in the laboratory fit Bohart-Adams equation on double logarithmic paper as a result of which a linear regression line emerges. This method helps engineers in designing ion exchange columns by means of similar operations.

Introduction

In chemical industries adsorption system has been used for many years and they significantly effect the cleaning up plant effluents and municipal waste waters. However, in practice, their design, plan and operation are rather tedious and time consuming. Hutchings [1,2] reported a method for designing granular activated carbon adsorption columns. He based the argument on the Bed Depth Service Time (BDST) concept His studies were based on an earlier simple but effective work by Eckenfelder [3]. All the investigations along this line are based on the Bohart and Adams [4] theory. Their theory expresses the relationship between the effluent concentration from an adsorption column and the service time

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{K \cdot N_0 \cdot X}{V} - K \cdot C_0 t \quad (1)$$

Where

C_0 : influent concentration of the ion for removal,

K : the adsorption rate coefficient.

N_0 : the adsorption capacity,

x : column length,

v : solution rate.

On the other hand, BDST equation can be rewritten succinctly in the form of a simple regression equation as $t = a + bx$.

It is obvious from eq. (1) that the breakthrough curve appears as S-shaped form asymptotically for large lines. Deep bed ion exchange columns lead to the same characteristic form and therefore, intuitively, it is possible to expect that the BDST and BA equations apply equally well in ion exchange process.

A simple regression type of equation has been developed in this paper for the ion exchange explanation for boric acid adsorption.

The BDST method is based on BA study but it does not yield satisfactory results without further modification. In its original form, the BA approach does not apply to ion exchange. Therefore, a more general approach by Thomas [5] in the analysis of adsorption processes is taken into consideration. A material balance equation is combined with a kinetic equation and its integration results in differential equation form for the adsorption expression. This general form includes the BA equation as a special case when appropriate assumptions are made. Similar to Thomas approach, the material balance equation is given as:

$$\frac{\partial q}{\partial t} + V \cdot \frac{\partial C}{\partial x} = 0 \quad (2)$$

where:

q : the deposited solids volume,

t : the service time measured from the beginning of the ion exchange run.

v: the rate,

χ : the depth of the ion exchange column

The kinetic equation is,

$$\frac{\partial q}{\partial t} = k_1(\varepsilon_0 - q)C - k_2q \quad (3)$$

where:

k_1 and k_2 : the attachment and detachment coefficients,

ε_0 : the ultimate capacity of the ion exchange.

Since $t = y/v$ and $df = qdx - cdy$ it is possible to obtain the kinetic expression by consideration from equation (2) and (3) as.

$$\frac{\partial^2 f}{\partial x \partial y} = \left(\frac{k_1 \varepsilon_0}{V}\right) \left(\frac{-\partial f}{\partial y}\right) - \left(\frac{k_1}{V}\right) \left(\frac{\partial f}{\partial x}\right) \left(\frac{-\partial f}{\partial y}\right) - \left(\frac{k_2}{V}\right) \left(\frac{\partial f}{\partial x}\right) \quad (4)$$

$$\left(\frac{C_0}{C} - 1\right) = \frac{\sqrt{\pi}[1 - \operatorname{erf}(\sqrt{r_1}t_1 - \sqrt{s})] \exp. (\sqrt{r_1}t_1 - \sqrt{s})^2 - (\sqrt{r_1}t_1 + \sqrt{r_1}st_1)^{-1}}{\sqrt{\pi}[1 - \operatorname{erf}(\sqrt{r_1}s - \sqrt{t_1})] \exp. (\sqrt{r_1}s - \sqrt{t_1})^2 - (\sqrt{t_1} + \sqrt{r_1}st_1)^{-1}} \quad (5)$$

The integrated form of the ion exchange relationship as obtained by Hiester and Vermeulen [6] is

See separate page

where r_1 , s and t_1 are integration constants and erf (x) represents the error function integration from zero up to the argument, x.

In this paper, r_1 , s and t_1 are defined as equilibrium, column capacity and solution capacity parameters as:

$$r_1 = \frac{k_2}{k_2 + k_1 C_0} \quad (6)$$

and

$$S = \frac{k_1 \varepsilon_0 X}{V} \quad (7)$$

$$t_1 = (C_0 k_1 + k_2) t \quad (8)$$

respectively. A close inspection of equation (5) indicates that in limit r_1 , t_1 and s attain the practical conditions. However some others become negligibly small in comparison to other terms. On the other hand it is possible to rewrite equation (6) as:

$$r_1 = \frac{1}{1 + \frac{k_1 C_0}{k_2}} \quad (9)$$

With all these consideration Eq. (5) can be written finally by taking logarithms as

$$\operatorname{Ln}\left(\frac{C_0}{C} - 1\right) = (r_1 - 1)(t_1 - s) \quad (10)$$

For ignarably small r_1 values

$$\operatorname{Ln}\left(\frac{C_0}{C} - 1\right) = (s - t_1) \quad (11)$$

Substituting s , from equation (7), and t_1 , from equation (8) into equation (11), gives

$$t = \frac{-\operatorname{Ln}\left(\frac{C_0}{C} - 1\right) \left(\frac{k_1 \varepsilon_0}{V}\right)}{(C_0 k_1 + k_2)} + \frac{\left(\frac{k_1 \varepsilon_0}{V}\right)}{(C_0 k_1 + k_2)} \quad (12)$$

If k_2 is much smaller than $C_0 k_1$, the last expression simplifies to,

$$\operatorname{Ln}\left(\frac{C_0}{C} - 1\right) = \left(\frac{k_1 \varepsilon_0}{V} - (C_0 k_1 t)\right) \quad (13)$$

Hence, the BA equation is written in terms of the ion exchange coefficients.

Table-1: Parameter calculated for a set of D and C_o values.

	Flow rate (ml/min)	k ₁ (cm ³ / gr.min)	ε _o (gr/cm ³)	-α	β (1/min)
D= 2 cm Co=1600 (mg/l)	1	11.87	3.5.10 ⁻²	5.03	0.02
	2	21.87	3.4.10 ⁻²	4.57	0.03
	3	41.87	2.4. 10 ⁻²	4.00	0.06
	4	36.87	3.6.10 ⁻²	4.06	0.06
	6	75.62	2.7.10 ⁻²	4.08	0.12
	7	81.87	2.4. 10 ⁻²	3.45	0.13
	10	85.00	3.0. 10 ⁻²	3.13	0.13
D= 5 cm Co= 1600 (mg/l)	1	75	6.0. 10 ⁻³	5.48	0.12
	2	137	5.8. 10 ⁻³	4.80	0.22
	3	270	4.0. 10 ⁻³	4.39	0.43
	4	213	6.1. 10 ⁻³	3.94	0.34
	6	575	3.7. 10 ⁻³	4.26	0.73
	7	596	4.0. 10 ⁻³	4.12	0.95
	10	573	5.0. 10 ⁻³	3.47	0.91
D= 10 cm Co= 500 (mg/l)	1	906	4.8. 10 ⁻⁴	5.18	0.45
	2	1816	4.5. 10 ⁻⁴	4.95	0.90
	3	3510	3.3. 10 ⁻⁴	4.57	1.75
	7	7214	3.2. 10 ⁻⁴	3.94	3.60
	10	7776	4.0. 10 ⁻⁴	3.70	3.88
D= 10 cm Co = 50(mg/l)	1	8200	5.0. 10 ⁻⁵	4.85	0.41
	2	14900	5.0. 10 ⁻⁵	4.37	0.74
	3	27860	3.0. 10 ⁻⁵	3.83	1.39
	7	64540	3.0. 10 ⁻⁵	3.66	3.22
	10	69120	4.0. 10 ⁻⁵	3.44	3.45

Table-2: Minimum column depth for a set of D and C_o values.

	Flow rate (ml/min)	X _{min} (cm)
D=2 cm C _o = 1600 mg/l	1	14.43
	2	16.12
	3	17.89
	4	18.05
	6	17.61
	7	21.34
	10	23.49
D=5 cm Co= 1600 mg/l	1	13.30
	2	15.07
	3	16.63
	4	18.44
	6	16.89
	7	17.58
	10	20.90
D= 10 cm Co= 500 mg/l	1	10.95
	2	11.79
	3	12.48
	7	14.61
	10	15.49
D= 10 cm Co= 50 mg/l	1	5.95
	2	6.55
	3	8.75
	7	8.82
	10	8.82

Results and Discussion

The shift in optimum pH depends upon surface properties of hydroxy compounds of metals.

However, no support for this hypothesis has been found. Although the optimum pH depends on both the nature of adsorbent and the solution, maximum boron removal is accomplished between pH 7.8 and 8.6 [10,11]. Laboratory studies indicated that boron can be removed from the waste waters of Boric acid and Borax plants by ion exchange.

A set of experimental data were obtained during the course of this study concerning the change of $\text{Ln} \left(\frac{C}{1-C} \right)$ with time. They are all similar, and therefore, for the sake of brevity representative samples are plotted in Figures 1-4. It is obvious from these figures that there are linear relationships between $\text{Ln} \left(\frac{C}{1-C} \right)$ and t. Such relationship are espacially pronounced for small operating times.

A similar analysis can be used in the design of deep bed ion exchange column and to investigate the effects on the varying depth service time of the ion exchange column, the ion exchange rate and the influent or the effluent concentrations. The coefficients also provide a basis for quantitative determination of the other process variable effects.

The ion exchange coefficient k₁ and ε_o, are the parameters of the breakthrough curve. The effects of the treatment on k₁ and ε_o can be determined by means of the BDST method, and the slope becomes

$$\text{slope} = \left(\frac{C_o - C}{C_o} \right) k_1 C \quad (14)$$

If the midpoint value for the concentration (C= 0.5 C_o) is substituted into equation (13), then service time can be expressed as.

$$t = \frac{\epsilon_o \cdot X}{C_o \cdot V} \quad (15)$$

This equation indicates that the midpoint displacement of the breakthrough curve from the origin will increase as the storage coefficient in addition to depth increase, and will decrease as the approach velocity and the influent concentration increase.

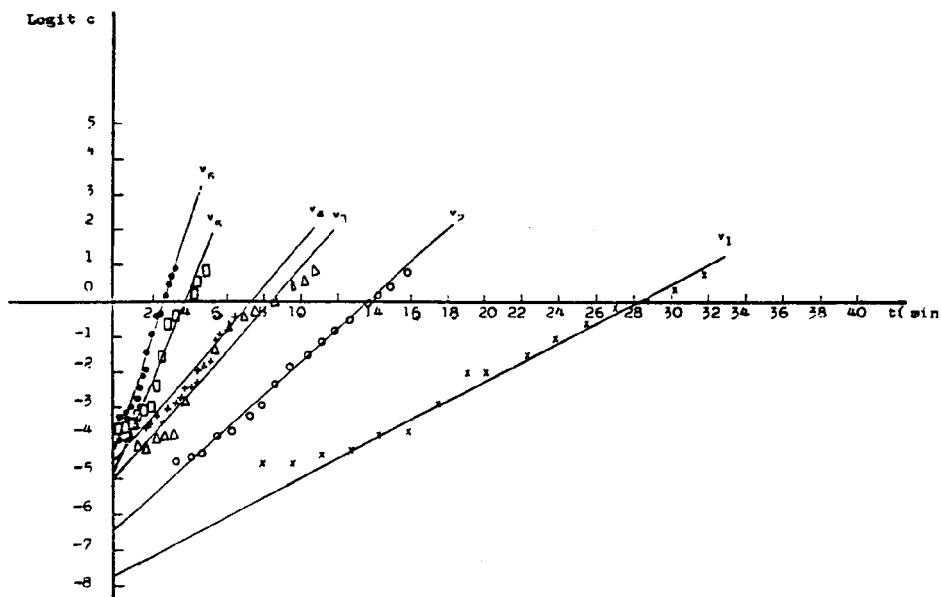


Fig. 1: Logit of c versus the service time ($D = 2$ cm, $C_0 = 1600$ mg/l)

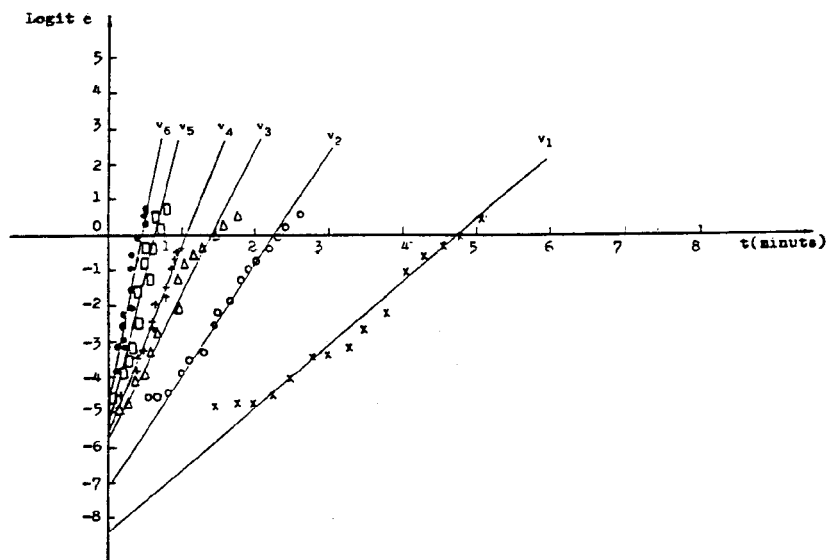


Fig. 2: Logit of c versus the service time ($D=5$ cm, $C_0 = 1600$ mg/l)

When the data are contained in a single breakthrough curve the BA equation can still be used in calculating the attachment. Hence, the use of short ion exchange column can be avoided and this in turn eliminates the need to use data. If s and t_1 are so small then they may affect the accuracy of coefficients calculated by using the BDST method.

Biologists have been using the inverse expression for many years in linearizing dose response relationship as follows.

$$\text{Ln}\left(\frac{c}{1-c}\right) = \alpha + \beta t \quad (16)$$

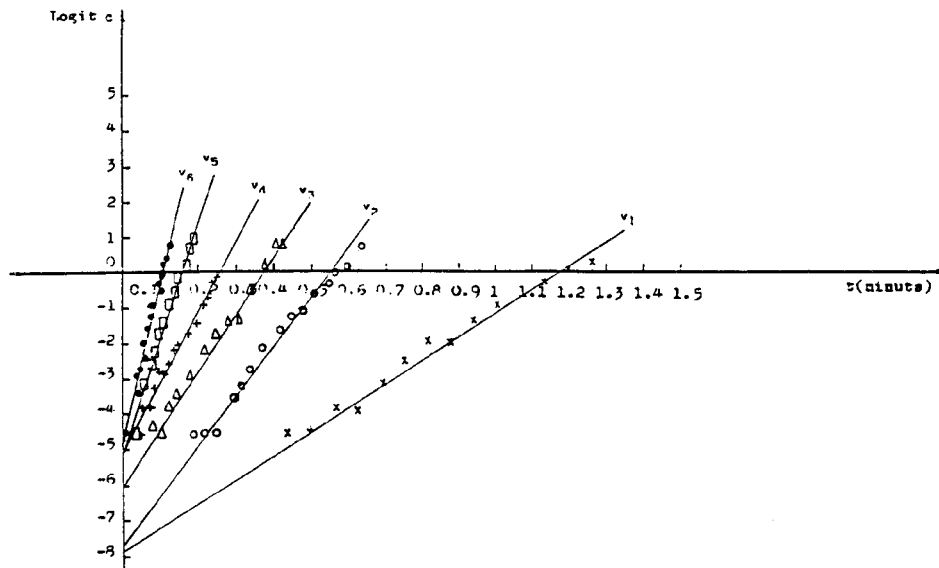


Fig. 3: Logit of c versus the service time (D=10 cm, C₀ = 500 mg/l)

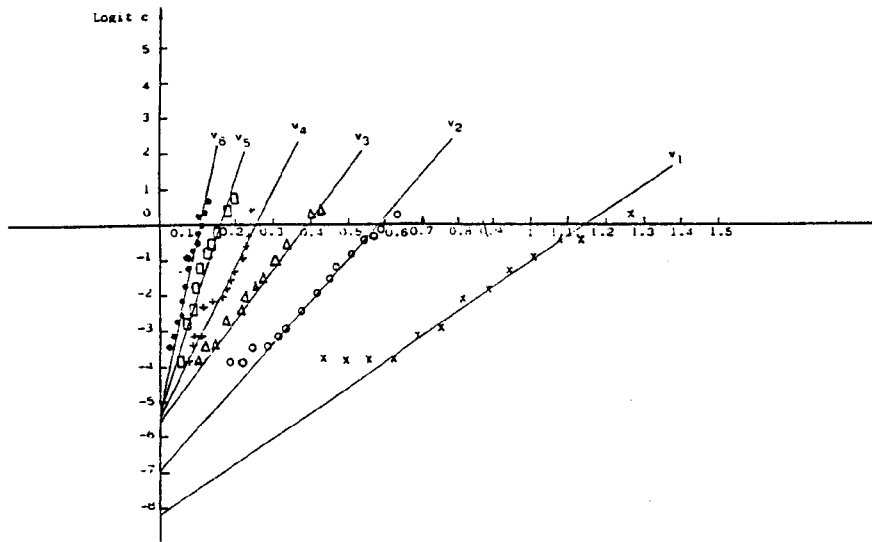


Fig. 4: Logit of c versus the service time (D=10 cm, C₀ = 50 mg/l)

where $\alpha = -k_1 \epsilon_0 x / V$, $\beta = k_1 C_0$ and $c = C/C_0$. The left hand side of this last equation is called the 'logit' of C/C_0 , which is a contraction in terms of 'logistical unit' [12,13]. The slope β in Eq. (16) is related to k_1 and C_0 as

$$k_1 = \frac{\beta}{C_0} \tag{17}$$

The storage coefficient is calculated using the intercept from the plot as,

$$\epsilon_0 = \frac{\alpha \cdot V}{k_1 \cdot X} \tag{18}$$

The experimentally calculated k_1 , ϵ_0 , α and β values are shown in Table-1. Comparison of various

blocks in this table leads to the following significant conclusions.

(1) It is obvious that change in C_o does not effect β significantly. Furthermore, β is solely dependent on the variations in D and not on C_o . So far as α values are concerned, there is a maximal 10% increase with the decrease of C_o from 500 to 50 mg/l for any given flow rate. Last but not the least, ϵ_o values differ by an order of 10.

(2). Different D values lead to increases in k_1 but the difference is not as pronounced when D is constant with varying C_o .

(3). Provided that D and C_o are constant then there are increase in k_1 and β with increasing flow rates. However, in the meantime, decrease occur in ϵ_o and also in α .

Based on the similar initial conditions equation (3) can be written for $q=0$ as,

$$\frac{\partial q}{\partial t} = \epsilon_o k_1 C \quad (19)$$

It is clear that the rate of deposition will be unaffected to the boron removal efficiency if the product of the coefficients remains the same.

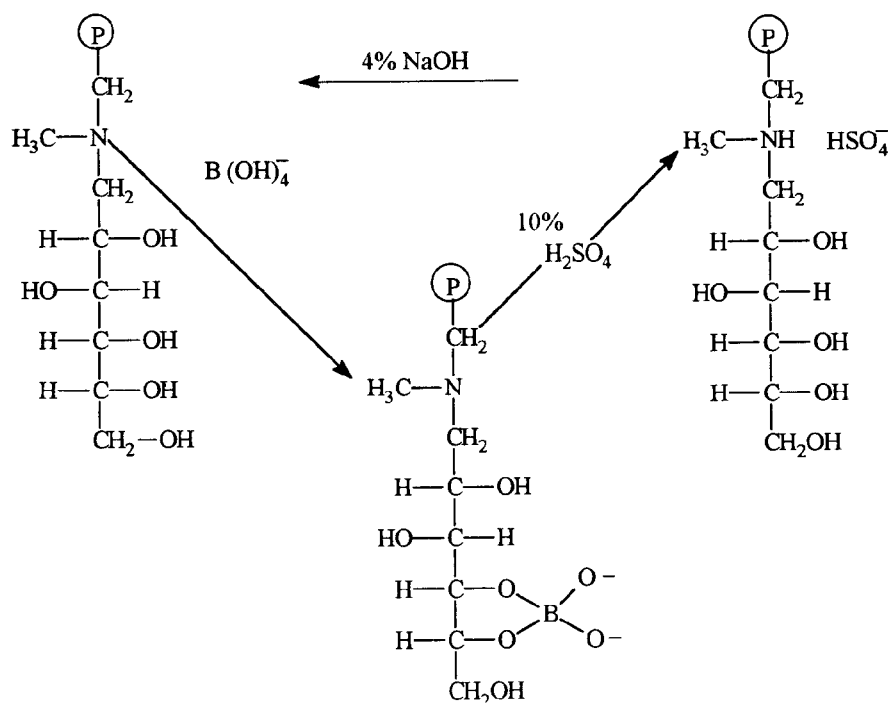
Solution of equation (12) for $t=0$ service time leads to the minimum attainable bed depth as

$$X_{\min} = \frac{V \cdot \ln\left(\frac{C_o}{C} - 1\right)}{k_1 \cdot \epsilon_o} \quad (20)$$

For different flow rates, X_{\min} values were calculated and results are shown in Table-2.

Experimental

Throughout this study, the waste waters of Boric acid and Borax plants were used as the source of boron. Daily amounts of these waters have been collected within a tank. The composite sample prepared in this tank, has been used in the laboratory studies. Samples with a concentration of approximately 500 mg/l were diluted with distilled water and subsequently a sample of 50 mg/l is



prepared. Following the determination of its concentration and adjustment of pH, experiments were conducted at room temperature ($23 \pm 2^\circ\text{C}$). The following scheme expresses. The loading and elution of the boron specific resin in free amine form is expressed as follows:

Laboratory experiments are conducted under the following circumstances:

a) The boron sorption was monitored as a function of pH after keeping the flow rate and the volume of resin in the column with the diameter of 10 cm the optimum pH was determined as 8.5.

b) At initial concentrations of 500 and 50 mg/l the boron sorption samples were passed at flow rates 1 to 10 cm^3/min through the column 2 and 10 cm diameters. The sorption ability of the resin decreased as the operation time of the column increased. Carminic acid reagent, and atomic absorption methods gave ability to determine the boron concentrations by a spectrophotometer [7-9].

Regeneration of resin was accomplished by 10% sulphuric acid solution. The acid residual left in the interstices of the resin was neutralized with 4% sodium hydroxide solution. The residuals are eliminated through the washing of column with distilled water.

Conclusions

For a given set of D and C_o values the minimum column lengths are calculated corresponding to another set of flow rates as shown in Table-2. Comparison of different blocks in this table leads to the following significant conclusions.

(1) For the same D and flow rates, decrease in C_o causes significant decreases in the minimum column depth.

(2) In general, for a given pair of D and C_o values, the minimum column depth increases with increasing flow rate but at a very flow rate.

(3) Whatever the flow rate is, for C_o constant any increase in D leads to decrease in the minimum column depth. On the other hand, if C_o is variable, then the change of χ_{min} is almost less than 15% in transition from D=2 cm to D=10 cm for $C_o=500$ mg/l.

References

1. A.R. Hutchings, *Ind. Wat. Engr.*, **10**, 40 (1973).
2. A.R. Hutchings, *Chem. Engr.*, **80**, 133 (1973).
3. W.W. Eckenfelder, *Industrial Water Pollution Control*, Mc Graw-Hill Book Co., New York (1966).
4. G.S. Bohart and E.Q. Adams, *J. Am. Chem. Soc.*, **42**, 523 (1920).
5. H.C. Thomas, *J. Am. Chem. Soc.*, **66**, 1664 (1944).
6. N.K. Hiester and T. Vermeulen, *Chem. Eng. Prog.*, **48**, 505 (1952).
7. Proposed Standard Methods for Boron Determination Committee Report, *J. AWWA*, **50**, 6 (1958).
8. Standard Methods for the Examination of Water and Wastewater, 14th Ed., APWA, AWWA (1997).
9. S. Sahin, *Chim. Act. Turc.*, **18**, 1 (1990).
10. W.W. Choi and K.Y. Chen, *Env. Scien. and Tech.*, **13**, 189 (1979).
11. A. Waggott, *Wat. Res.*, **3**, 749 (1969).
12. J. Berkson, *J. Am. Stat. Assoc.*, **39**, 357 (1944).
13. S. Sahin, *J. Chem. Soc. Pak.*, **14**, 3 (1992).