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Statistical Modeling of Lead (Pb) Adsorption on Van Pumice

Canan Demir*, Yıldırım Demir, Ali Rıza Kul, Halime Yıldız

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Abstract: The aim of this study is to statistical modeling of lead (Pb) adsorption on Van Pumice. Van Pumice was used for determination of lead (Pb) adsorption level. Modeling, depending on time, was performed to determine for lead (Pb) adsorption level at fixed pH 5.5 for various concentration and temperatures in Van pumice. All adsorption measurements were performed with the Thermo Scientific brand ICE spectrometer model 300 Series. One-way analysis of variance was used for comparison to various temperature and concentration levels. Tukey's multiple comparison test was also performed to determine different groups. Logarithmic, quadratic, cubic and logistic models as well as linear were used to determine adsorbed lead (Pb) amount at different temperature levels and heavy metal concentration. Differences between various time and concentration levels were found statistically significant; however, there were no significant differences between temperature and concentration levels. In addition, cubic model had higher R^2 values for each concentration and temperature levels. Lead (Pb) concentration and amount of ions have been increased in the solution. As a result, although all models were significant, cubic model showed the best performance.

Keywords: Lead (Pb), Adsorption, Logarithmic, Logistic Modeling.

INTRODUCTION

Lead (Pb) is a heavy metal commonly found in nature. Heavy metals are metals with a density greater than 5 g / cm-3 [1]. Heavy metals do not degrade and cannot be destroyed. Lead is a toxic element that threatens the environment and health because while urbanization and industrialization have increased rapidly in industrialized societies, the necessary measures have not been taken at the same rate [2]. Lead is used as an industrial raw material in oil industry, printing industry, accumulators and cars and in the production of various machinery and equipment, plumbing equipment, fuels, matches, photograph materials, explosives, weapons, in the production of x-ray shielding materials for the field of medicine and as a covering material. Waste water from these industries contains lead in unwanted concentrations [3]. The lead taken to the human body in various ways such as inhalation, nutrients and water is distributed primarily to the soft tissues and parenchymal organs and then stored in the bones by replacing calcium. It is reported that it affects many systems and organs such as hematologic system, central nervous system, kidneys and liver [4].

Due to its high toxicity, the adsorption of lead is of great importance for both environmental and human health. Adsorption is a separation process that is based on transferring of atoms ions or molecules in the solution medium to an adsorbent surface and often occurs in the surface phase. Adsorption is described as hold of the atom, ions or molecules on a solid surface. Desorption is expressed as separation of hold particles on the surface. Similarly, solid is called adsorptive (adsorbent) and keep the material on the solid surface is called adsorbed (soluble) [5].

The effect of temperature on the adsorption depends on being of adsorption exothermic or endothermic.

Canan Demir*, Yuzuncu Yıl University, Vocational School of Health Care, Van-TURKIYE. E-mail: canantasin@gmail.com
Yıldırım Demir, Yuzuncu Yıl University, Faculty of Economics and Administrative Sciences, Department of Statistics, Van-TURKIYE.
Ali Rıza Kul, Yuzuncu Yıl University, Vocational School of Health Care, Van-TURKIYE.
Halime Yıldız, Yuzuncu Yıl University, Vocational School of Health Care, Van-TURKIYE.

Increasing of temperature causes reducing amount of adsorbed material in case of exothermic adsorption, however lead to increase in case of endothermic adsorption. By the rising of temperature, increasing amount of adsorbed substances depends on dissolution of adsorbed species, the change in the pore structure and increasing of diffusion rates for the adsorbed particles [6]. Adsorption is an equilibrium process and lasts until form a dynamic balance between concentration of solute remaining in solution and concentration of hold on the surface [5; 7; 8].

One of the substances used as adsorbent material is pumice. Pumice is very common in Van and more economical than other adsorptive substances. In case of using pumice as an adsorbent agent, determination of the amount for adsorbed lead at different concentrations (25, 35, 45ppm) and temperatures (25, 35, 45 °C) is important.

Although many studies have been conducted about change of adsorbed substances amount to temperature and time, it can be said that studies on modeling of these substance amount with regard to time and temperature are not sufficient. Therefore, in addition to the linear regression model, four nonlinear regression models were performed to obtain estimation equations and to determine the usability of these equations.

EXPERIMENTAL

Van Pumice was used for adsorption studies in the experimental stage.

Washing process of pumice: Van Pumice grinded in the mill and passed through a sieve with 230 mesh were dried in the oven for 5.5 hours. 100 grams Van Pumice was mixed with 1.7 liters pure water in the mixer for 12 hours.

After completion of mixing, it was kept waiting for 12 hours. It was observed that the solid phase was separated from aqueous phase. The solid phase was separated by filtration. In order to dry, the solid phase was allowed to stand at room temperature for 168 hours. Dried Van pumice was again passed sieve with 230 mesh. With putting into the storage containers, it was placed in the desiccators for use in the experiment.

1 gram of pumice in the adsorption equilibrium studies was treated with 300 mL of heavy metal solutions.

Prepared heavy metal solutions (Pb) in 25ppm, 35ppm and 45ppm concentrations and at pH 5.5 were shaken with Van pumice at different temperatures (25^{o}C, 35^{o}C, 45^{o}C) and time periods (5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80, 90, 100, 120, 140, 160, 180, 200, 240 min).

Pb adsorption in Van Pumice example was examined by depending on concentration, temperature and time at pH 5.5.

All adsorption measurements were performed by Thermo Scientific brand the 300 Series II models to a spectrometer [9].

Statistical Analysis: Regression is expressed as a function of independent variables thought to be associated with the dependent variable. The functional form of the relationship between variables is examined by regression models.

The regression model that should be used differs according to the structure of the data. Using the wrong model can lead to erroneous results.

The general expression of the regression equation is written as follows [10].

$$Y= \beta_0 + \beta_1 X+ \varepsilon \qquad (1)$$

Y: Dependent (result) variable is assumed to have a certain error

X: Independent (cause) variable is assumed to be measured without error

β_0: Y is the value that is when X = 0. It is the point where the line breaks the y-axis

β_1: It is the slope of the line or the regression coefficient. X refers to the amount of change in Y when a unit changes

ε: It is the random error value [11].

Least Squares Method: The most commonly used method for estimating the regression coefficients is the least squares method. Least squares method is based on finding a curve equation so that the sum of squares of errors will be minimum.

$$Min\sum e_i^2 = \sum\left(Y - (\beta_0 + \beta_1 X)\right)^2 \quad (2)$$

For minimum of a second order function derivative are equalized to zero. Accordingly, regression constant and regression coefficient are obtained as follows. [12].

$$\beta_0 = \bar{Y} - \beta_1 \bar{X}$$

$$\beta_1 = \frac{\sum(Y-\bar{Y})(X-\bar{X})}{\sum(X-\bar{X})^2}$$

Descriptive statistics for the studied variables were expressed as mean , standard deviation , minimum and maximum values.

Variance analysis (ANOVA) was used to determine whether there was a difference between both time and temperature levels for three concentrations. In order to identify different groups, Tukey's multiple comparison test was used following ANOVA. In addition, logarithmic, quadratic, cubic and logistic models as well as linear model were used to estimate the amount of adsorbed heavy metals at different temperatures and heavy metal concentrations.

Linear; $Y = a_0 + a_1X$

Logarithmic; $Y = a_0X^{a_1} => lnY = a_0 + a_1lnX$

Quadratic; $Y = a_0 + a_1X + a_2X^2$

Cubic; $Y = a_0 + a_1X + a_2X^2 + a_3X^3$

Logistic; $Y = a_0 + a_1(logX) + a_2(logX)^2$

Accordingly, the most properly model was determined and the approximate curves representing the model on the spread diagrams were shown [13].

R-square (R^2, Determination coefficient) was considered to determine goodness of fit the models. Level of significance was taken 5% for all statistical tests and comparisons and SPSS statistical software was used for the all statistical computations.

FINDINGS

For lead ions, descriptive statistics of adsorption on Van Pumice and comparison results are given in **Table 1** by depending on concentration (25ppm, 35ppm, 45ppm) and time.

As seen in **Table 1**, difference between the times for each concentration was found to be statistically significant ($p<0.01$).

Accordingly, when lead ion shaken for 5 minutes, average adsorption amount was 4.47 in 25ppm concentration however, average concentration was 16.83 when it shaken for 240 minutes in the same concentration.

Similarly, at 35ppm, when shacked for 5 min, the average was 8.61, while it was found 23.28 by increasing of shaking duration to 240 minutes in the same concentration. When lead ions concentration was 45ppm, adsorbed amount of the substance was 8.98 for 5 min shaking duration, however, this value reached to 30.64 for 240 min shaking duration.

By depending on the temperature and concentrations (25ppm, 35ppm, 45ppm), descriptive statistics of adsorbed lead ions on Van pumice and comparison results are given in **Table 2**. When **Table 2** is examined; there are no differences among the amounts of temperature levels (25°C, 35°C, 45°C) for adsorption on Van Pumice of lead ions in different concentrations.

Table 1: Descriptive statistics and comparison results of absorbance values for various time intervals

ppm	Time	N	Mean	S.D.	Min	Max	p
25	5	3	4.47	0.59	3.81	4.96	0,001
	10	3	6.35	1.26	4.93	7.33	
	15	3	7.08	1.30	5.60	8.04	
	20	3	8.80	2.33	6.19	10.67	
	25	3	10.72	1.86	8.63	12.21	
	30	3	12.14	1.43	10.67	13.53	
	40	3	13.97	0.64	13.33	14.61	
	50	3	14.68	0.69	14.03	15.41	
	60	3	15.12	0.89	14.12	15.81	
	70	3	15.48	1.11	14.21	16.26	
	80	3	15.95	1.55	14.33	17.41	
	90	3	16.82	1.13	15.61	17.86	
	100	2	16.83	1.11	15.65	17.85	
	120	3	16.84	1.11	15.66	17.87	
	140	3	16.84	1.12	15.65	17.88	
	160	3	16.83	1.12	15.64	17.87	
	180	3	16.84	1.13	15.63	17.86	
	200	3	16.82	1.12	15.62	17.85	
	240	3	16.83	1.13	15.63	17.87	
35	5	3	8.61	2.08	6.49	10.64	0,001
	10	3	10.80	1.32	9.62	12.23	
	15	3	12.48	1.30	11.21	13.81	
	20	3	14.18	0.71	13.66	14.99	
	25	3	15.63	0.59	15.28	16.31	
	30	3	17.55	1.13	16.41	18.67	
	40	3	18.88	0.36	18.67	19.29	
	50	3	19.53	0.26	19.26	19.78	
	60	3	21.24	0.62	20.64	21.88	
	70	3	21.93	0.94	20.99	22.86	
	80	3	22.33	1.16	21.11	23.41	
	90	3	23.24	1.69	21.43	24.78	
	100	3	23.26	1.69	21.45	24.79	
	120	3	23.27	1.70	21.44	24.81	
	140	3	23.27	1.72	21.43	24.83	
	160	3	23.27	1.71	21.44	24.82	
	180	3	23.27	1.72	21.44	24.84	
	200	3	23.26	1.72	21.43	24.83	
	240	3	23.28	1.70	21.46	24.82	
45	5	3	8.98	2.98	5.87	11.81	0,001
	10	3	12.20	1.42	11.28	13.83	
	15	3	15.85	0.97	14.88	16.81	
	20	3	17.98	1.30	16.86	19.41	
	25	3	20.02	3.07	17.33	23.36	
	30	3	23.63	1.82	22.49	25.73	
	40	3	25.93	1.27	24.81	27.31	
	50	3	27.14	1.68	25.33	28.66	
	60	3	28.54	1.40	26.99	29.73	
	70	3	29.34	0.81	28.61	30.21	
	80	3	29.98	1.02	28.96	30.99	
	90	3	30.62	0.66	29.99	31.31	
	100	3	30.63	0.66	30.02	31.33	
	120	3	30.64	0.68	30.00	31.35	
	140	3	30.63	0.67	29.99	31.32	
	160	3	30.65	0.69	29.99	31.36	
	180	3	30.61	0.66	29.98	31.29	
	200	3	30.64	0.65	30.03	31.32	
	240	3	30.64	0.65	30.05	31.33	

When **Table 2** is examined; there are no differences among the amounts of temperature levels (25°C, 35°C, 45°C) for adsorption on Van Pumice of copper ions in different concentrations.

Table 2: Descriptive statistics and comparison results of absorbance values for various temperatures

ppm	°C	N	Mean	Sd	Min	Max	p
25	25	19	13.04	3.46	4.64	15.66	0.710
	35	19	14.18	3.79	4.96	17.03	
	45	19	13.73	5.26	3.81	17.88	
35	25	19	18.38	4.66	6.49	21.46	0.445
	35	19	19.50	5.01	8.69	23.56	
	45	19	20.42	5.02	10.64	24.84	
45	25	19	24.41	7.48	5.87	30.05	0.699
	35	19	25.82	6.88	9.26	30.59	
	45	19	26.29	6.87	11.81	31.36	

Table 3: Model Summary and Parameter Estimates

ppm	Heat (°C)	Models	R^2	Constant	b1	b2	b3
25	25	Linear	0.77**	7.672**	0.537**		
		Logarithmic	0.96**	4.379**	4.185**		
		Quadratic	0.97**	3.643**	1.689**	-0.058**	
		Cubic	0.99**	2.214**	2.450**	-0.150**	0.003**
		Logistic	0.67**	0.133**	0.951**		
	35	Linear	0.77**	8.273**	0.591**		
		Logarithmic	0.96**	4.656**	4.599**		
		Quadratic	0.98**	3.817**	1.864**	-0.064**	
		Cubic	0.99**	2.386**	2.626**	-0.157**	0.003**
		Logistic	0.67**	0.124**	0.950**		
	45	Linear	0.82**	5.298**	0.844**		
		Logarithmic	0.91**	0.883**	6.207**		
		Quadratic	0.97**	-0.031**	2.366**	-0.076**	
		Cubic	0.97**	0.751**	1.949**	-0.025**	-0.002**
		Logistic	0.75**	0.180**	0.923**		
35	25	Linear	0.70**	11.479**	0.690**		
		Logarithmic	0.93**	6.841**	5.575**		
		Quadratic	0.97**	5.295**	2.457**	-0.088**	
		Cubic	0.99**	2.556**	3.917**	-0.266**	0.006**
		Logistic	0.61**	0.091**	0.954**		
	35	Linear	0.83**	11.376**	0.813**		
		Logarithmic	0.96**	6.937**	6.070**		
		Quadratic	0.99**	6.234**	2.282**	-0.073**	
		Cubic	0.99**	6.107**	2.350**	-0.082**	0.000**
		Logistic	0.77**	0.087**	0.953**		
	45	Linear	0.88**	12.052**	0.837**		
		Logarithmic	0.93**	8.018**	5.989**		
		Quadratic	0.98**	7.961**	2.005**	-0.058**	
		Cubic	0.99**	9.496**	1.188**	0.041**	-0.003**
		Logistic	0.84**	0.080**	0.956**		
45	25	Linear	0.78**	12.658**	1.176**		
		Logarithmic	0.96**	5.598**	9.087**		
		Quadratic	0.98**	4.051**	3.634**	-0.123**	
		Cubic	0.99**	2.059**	4.696**	-0.252**	0.004**
		Logistic	0.65**	0.082**	0.939**		
	35	Linear	0.72**	15.416**	1.041**		
		Logarithmic	0.94**	8.688**	8.275**		
		Quadratic	0.97**	6.667**	3.540**	-0.125**	
		Cubic	0.99**	3.212**	5.381**	-0.349**	0.007**
		Logistic	0.63**	0.067**	0.951**		
	45	Linear	0.78**	15.535**	1.075**		
		Logarithmic	0.92**	9.379**	8.167**		
		Quadratic	0.98**	7.683**	3.319**	-0.112**	
		Cubic	0.98**	7.195**	3.579**	-0.144**	0.001**
		Logistic	0.73**	0.064**	0.953**		

In order to determine the adsorption of lead ions on Van pumice, results of the used models are given in **Table 3**. As seen **Table 3**, cubic model with 99% R^2value was the best model for 25ppm and 25°C temperature. This model was followed by quadratic model with 97%, logarithmic model with 96% and linear model with 77% R-square values. The logistic model was the last with 67%. Cubic model was also the best model with 99% R^2 value at 35°C.

This model was followed by quadratic model with 98%, logarithmic model with 96% and linear model with 77% R^2 value. The logistic model was included in last with 67%. When temperature was 45°C, the best estimations were made by cubic and quadratic models with 97% R^2 value. These models were followed by logarithmic model with 91% and linear model with 82% R-square value. The lowest estimation was made by logistic models with 75% R^2 value.

When we look at the table values to 35ppm and 25 ° C temperature, cubic model were the best models with 99% R-square value. This was followed by quadratic model with 97%, logarithmic model with 93%, linear model with 70% and logistic model with 61%. For the same concentration and 35°C temperature, Cubic and quadratic models had the highest predictive value with 99% R-square value. R-square values for logarithmic, linear and logistic models were found 96%, 83% and 77%, respectively. Similarly, for the same concentration and for the 45°C temperature, cubic model had the highest (99%) value. This model was followed by the quadratic model with 98%, logarithmic model with 93%, linear model with 88% and logistic model with 84% R-square value.

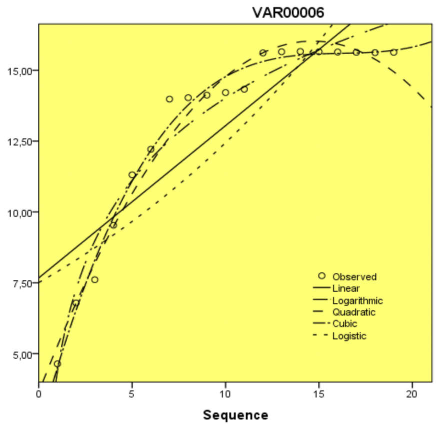

Figure 1: Pb 25ppm 25^0C

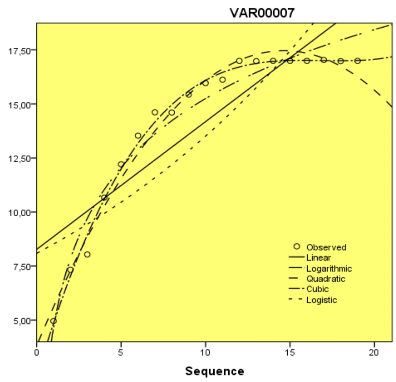

Figure 2: Pb 25ppm 35^0C

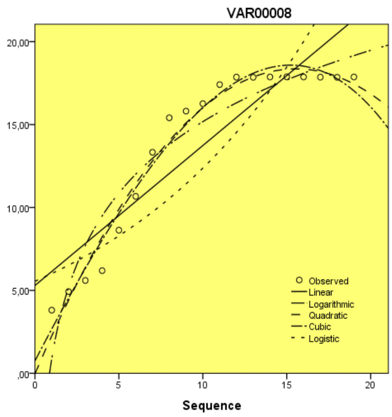

Figure 3: Pb 25ppm 45^0C

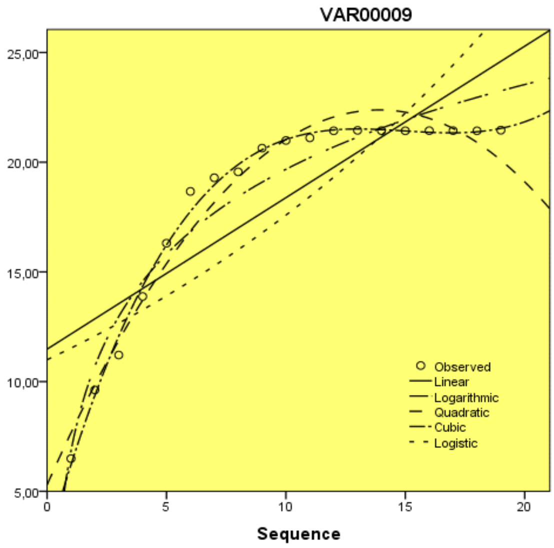

Figure 4: Pb 35ppm 25^{0}C

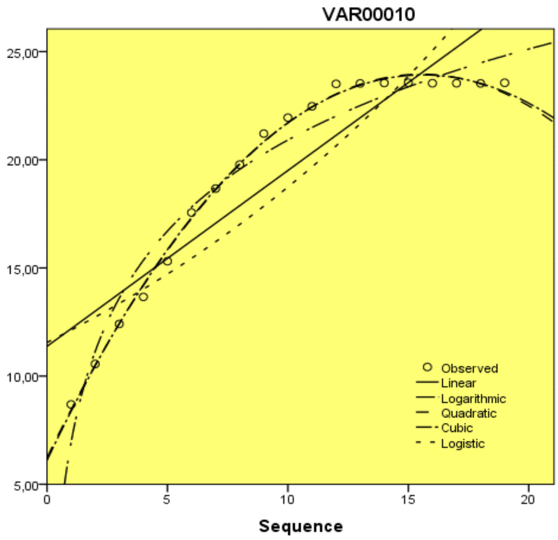

Figure 5: Pb 35ppm 35^{0}C

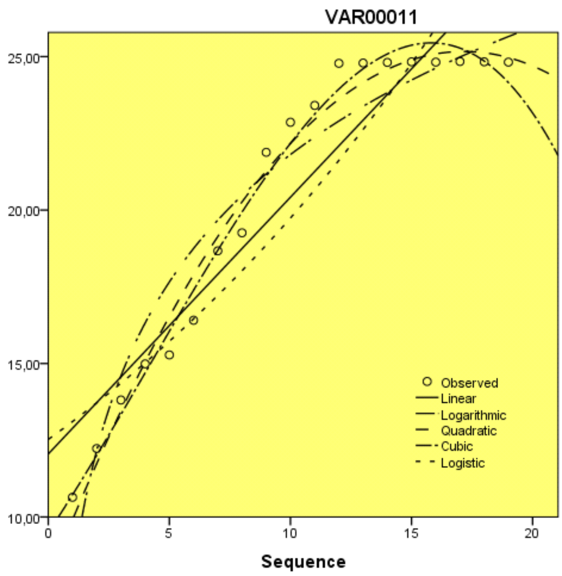

Figure 6: Pb 35ppm 45^{0}C

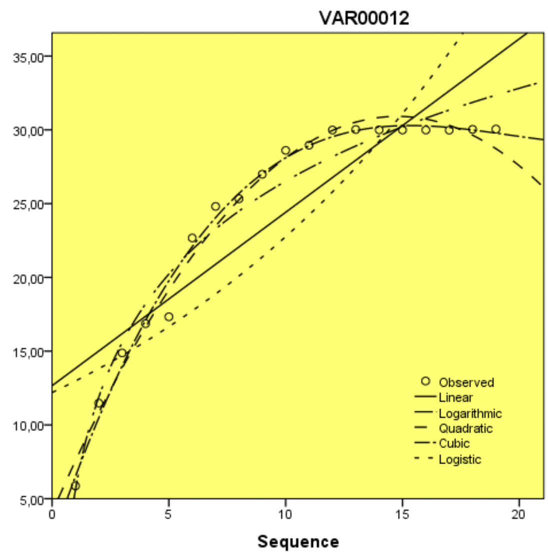

Figure 7: Pb 45ppm 25^0C

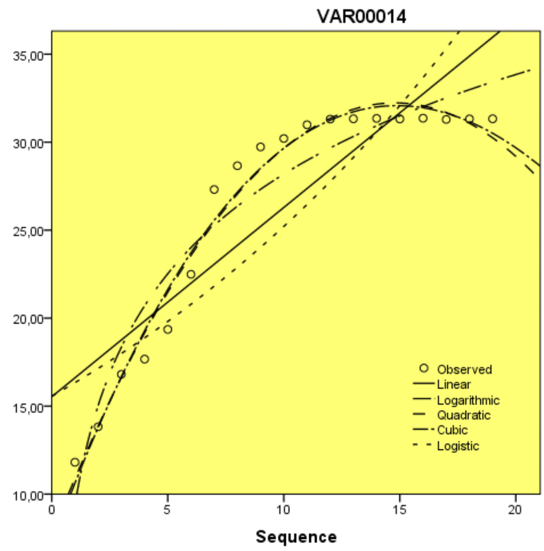

Figure 9: Pb 45ppm 45^0C

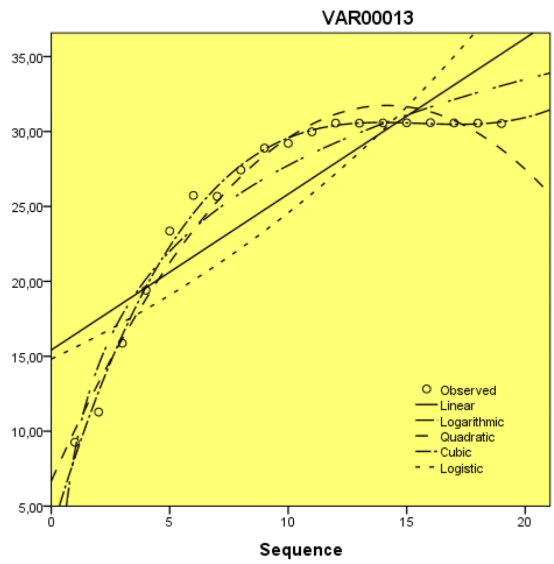

Figure 8: Pb 45ppm 35^0C

DISCUSSION AND CONCLUSIONS

In this study, the adsorption of lead ions on Van pumice were examined at various temperatures (25^{o}C, 35^{o}C, 45^{o}C), time (5, 10, 15,…,240 min) and (25ppm, 35ppm, 45ppm) concentrations. Based on the data provided in **Table 1** which shows the comparison results of the adsorption durations of lead ions on the Van Pump, the difference between the durations for each concentration was found statistically significant ($p<0.001$). Adsorption increased directly by proportional mixing time and this increase was fast in the first minutes, then this stabilized quickly. Similar results were reported by [6; 14; 15; 16; 17; 18; 19; 20]. Based on the data provided in **Table 2** which shows the comparison results of the adsorption of lead ions in terms of temperature levels on the Van Pump, It was observed that the adsorption efficiency did not change with temperature. Based on the result in **Table 3** to determine the adsorption of lead ions on the Van Pump; the models having the highest estimation coefficient of determination (R^2) and the lowest standard error values were indicated as the most appropriate models. Both for all temperature values (25^{o}C, 35^{o}C, 45^{o}C) and for all concentrations (25ppm, 35ppm, 45ppm), cubic and quadratic models provided the best estimation of the R^2 value which ranges from 96% to 99%. This model was followed by logarithmic model which varies from 91% to 96% R^2 value, linear model which varies from 70% to 88% R^2 value and logistic model which varies from 61% to 84% R^2 value.

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