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Statistical Modeling of Cobalt Adsorption on Van Pumice

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ABSTRACT

The aim of this study is to statistical modeling of cobalt adsorption on Van Pumice. Van Pumice was used for determination of cobalt adsorption level. Modeling, depending on time, was performed to determine for cobalt adsorption level at fixed pH 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, Qubic and logistic models as well as linear were used to determine adsorbed cobalt amount at different temperature levels and heavy metal concentration. Differences between various time and temperatures levels were found statistically significant, however, there were no significant differences between time level. R^2 values of the models ranged from 70% to 99%. In addition, cubic model had higher R^2 values for each concentration and temperature levels. Cobalt concentration and amount of ions have been increased in the solution. The performance of all models to determine the amount of adsorption of cobalt has been significantly found. However, model the best performance has been shown with the cubic.

Keywords: Co, adsorption, logarithmic, logistic models

INTRODUCTION

Heavy metals may spread the environment from various sources. The firs one of these resource is daily activities of people. Consumption of solid fuel containing a large amount of heavy metals, exhaust emissions, industrial and household waste as well as mining activities and industrialization are among the main causes of serious heavy metal pollution [1]. Cobalt is solid structure and formed during the production of lead and tin mines that is non-melting and prevents the use of metal. Cobalt is in the least elements group of Earth with 25 mg / ton average value. Cobalt has important applications areas such as military, strategic and industrial. The most using type of cobalt is as super alloys in jet engine turbine. In addition, cobalt is also used to provide the magnetism properties for materials, protect from corrosion, and improve the mechanical properties in alloys, speed steel, tool steel, diamond tools, and cutting edge.

Although, there are no certain findings about that cobalt and cobalt compounds cause cancer in humans, it has been noted that these compounds are carcinogen substances [2].

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 occur 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 from the surface. Similarly, solid is called adsorptive (adsorbent) and keep the material on the solid surface is called adsorbed (soluble) [3]. The effect of temperature on the adsorption depends on being of adsorption exothermic or endothermic. Increasing of temperature causes

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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 [4]. 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 [3, 5, 6]. Although many studies have been conducted about change of adsorbed substances amount to temperature and time, the studies about modeling of these substance amount with regard to time and temperature have been rare. 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 cobalt at different concentrations (50, 75, 100 ppm) and temperatures (25, 35, 45 °C) is important. Therefore, using four nonlinear statistical models as well as linear model were performed to obtain estimation of the curves and to determine the availability of these models.

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.

Van pumice was grinded in the mill and then particle size was made smaller by passing through a sieve with 230 mesh. 1 gram of pumice in the adsorption equilibrium studies was treated with 300 mL of heavy metal solutions. Prepared heavy metal solutions (Co) in 50 ppm, 75 ppm and 100 ppm concentrations and at pH 5 were shaken with Van pumice at different temperatures (25 °C, 35 °C, 45 °C) and time periods (5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 150, 180 min).

Co adsorption in Van Pumice example was examined by depending on concentration, temperature and time at pH 5. All adsorption measurements were performed by Thermo Scientific brand the 300 Series II models to a spectrometer.

Statistical Analysis

Descriptive statistics for the studied variables were expressed as Mean, Standard deviation, Minimum and Maximum values. For the comparisons based on temperature and time, one-way analysis of variance (One way-ANOVA) was used. In order to identify different groups, Tukey's multiple comparison test was used following ANOVA. In addition, Logarithmic, Quadratic, Qubic 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.

R-squared (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 cobalt ions, descriptive statistics of adsorption on Van Pumice and comparison results are given in **Table 1** by depending on concentration (50 ppm, 75ppm, 100ppm) 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 cobalt ion shaken for 5 minutes, average adsorption amount was 10.01 in 50 ppm concentration however, average concentration was 38.88 when it shaken for 180 minutes in the same concentration. Similarly, at 75 ppm, when shaked for 5 min, the average was 19.45, while it was found 61.69 by increasing of shaking duration to 180 minutes in the same concentration. When cobalt ions concentration was 100 ppm, adsorbed amount of the substance was 24.31 for 5 min shaking duration, however, this value reached to 84.08 for 180 min shaking duration.

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

	Time	N	Mean	S.D.	Min	Max	P
ppm50.Co	5	3	10.01^{g}	.24	9.87	10.28	0.001
	10	3	13.42^{fg}	1.57	11.75	14.85	
	15	3	15.55^{fg}	2.32	13.89	18.20	
	20	3	18.68^{efg}	4.57	15.27	23.87	
	25	3	22.76^{def}	3.12	19.59	25.81	
	30	3	25.25^{cde}	4.51	20.88	29.88	
	40	3	26.76^{cde}	5.02	22.00	32.00	
	50	3	28.75^{bcd}	5.53	22.89	33.87	
	60	3	30.51^{abcd}	5.62	24.67	35.87	
	70	3	34.21^{abc}	5.13	29.88	39.87	
	80	3	37.48^{ab}	5.73	31.00	41.87	
	90	3	38.71^{a}	6.24	31.79	43.88	
	110	3	38.87^{a}	6.92	31.08	44.26	
	120	3	38.89^{a}	6.93	31.08	44.30	
	150	3	38.89^{a}	6.93	31.08	44.30	
	180	3	38.88^{a}	6.92	31.08	44.26	
ppm75.Co	5	3	19.45^{g}	5.33	14.25	24.89	0.001
	10	3	26.38^{fg}	7.67	19.99	34.89	
	15	3	31.07^{efg}	12.17	21.90	44.87	
	20	3	35.08^{defg}	10.68	24.50	45.87	
	25	3	40.90^{cdef}	8.89	34.27	51.00	
	30	3	43.70^{bcde}	9.83	36.37	54.87	
	40	3	46.84^{abcde}	8.33	39.71	56.00	
	50	3	48.86^{abcd}	7.94	42.89	57.88	
	60	3	50.71^{abcd}	8.06	44.50	59.82	
	70	3	55.00^{abc}	9.11	45.98	64.20	
	80	3	57.09^{abc}	9.20	47.00	65.00	
	90	3	58.87^{ab}	9.18	48.86	66.88	
	110	3	61.69^{a}	7.72	52.88	67.28	
	120	3	61.70^{a}	7.73	52.88	67.30	
	150	3	61.70^{a}	7.73	52.88	67.30	
	180	3	61.69^{a}	7.72	52.88	67.29	
ppm100.Co	5	3	24.31^{i}	2.38	22.00	26.76	0.001
	10	3	30.85^{hi}	2.62	27.87	32.80	
	15	3	40.49^{gh}	.58	39.82	40.86	
	20	3	48.86^{fg}	5.60	42.82	53.89	
	25	3	55.70^{ef}	4.49	50.96	59.89	
	30	3	61.92^{de}	2.60	60.00	64.87	
	40	3	66.78^{cd}	2.12	65.28	69.21	
	50	3	71.32^{bcd}	3.83	67.00	74.32	
	60	3	75.36^{abc}	6.15	68.36	79.88	
	70	3	77.00^{abc}	6.08	70.00	81.00	
	80	3	80.02^{ab}	7.38	71.89	86.28	
	90	3	82.02^{ab}	8.91	72.33	89.86	
	110	3	84.04^{a}	7.86	75.64	91.21	
	120	3	84.09^{a}	7.78	75.78	91.21	
	150	3	84.09^{a}	7.78	75.78	91.21	
	180	3	84.08^{a}	7.79	75.77	91.21	

a,b,c: Different lower cases represent different group means ($p<0.001$)

For various temperature and concentrations (50 ppm, 75 ppm, 100ppm), descriptive statistics of adsorbed cobalt ions on Van pumice and comparison results are given in **Table 2**.

When **Table 2** is examined; for 50 ppm concentrations, 23.61 amount of substance in adsorption at 25 °C temperature, at 45 °C temperature, 32.94 amount of substance in adsorption. Alike, at 75 ppm concentrations, 39.48 amount of substance in adsorption at 25 °C temperature, at 45 °C temperature 55.96 amount of substance in adsorption. For 95 ppm concentrations, there was no statistically significant difference among temperature levels.

Table 2. Descriptive statistics and comparison results of absorbance values for various temperature

	°C	N	Mean	Sd	Min.	Max.	p
ppm.50	25	16	23.61 b	7.77	9.87	31.79	.045
	35	16	29.26 ab	11.16	10.28	41.29	
	45	16	32.94 a	11.52	9.87	44.30	
ppm.75	25	16	39.48 b	12.98	14.25	52.88	.007
	35	16	47.20ab	15.69	19.20	64.92	
	45	16	55.96 a	12.81	24.89	67.30	
ppm.100	25	16	61.52a	15.97	26.76	75.78	0.53
	35	16	65.86a	21.33	24.18	85.27	
	45	16	69.67a	23.11	22.00	91.21	

In order to determine the adsorption of cobalt ions on Van pumice, results of the used models are given in **Table 3**. As seen **Table 3**, cubic model with 98% R^2 value was the best model for 50 ppm and 25 °C temperature. This model was followed by quadratic model with 97%, logarithmic model with 94% and linear model with 74% R-square values. The logistic model was the last with 69% R-square values.

When temperature was 35 °C, the best estimations were made by cubic and quadratic models with 98% R^2 value. These models were followed by logarithmic model with 95% and linear model with 79% R-square value. The lowest estimation was made by logistic models with 74% R^2 value.

When temperature was 45 °C, the best estimation were made by cubic models with 98% R^2 value. These models were followed by logarithmic model with 97%, quadratic model with 96% and linear model with 73% R-square value. The lowest estimation was made by logistic models with 66% R^2 value.

When **Table 3** was examined for 75 ppm concentration and 25 °C temperature, cubic model were the best model with 98% R-square value. This was followed by logarithmic model with 97%, quadratic model with 95%, linear model with 74% and logistic model with 70%.

For the same concentration and 35 °C temperature, cubic model had the highest predictive value with 99% R-square value. R-square values for quadratic, logarithmic, logistic and linear models were found 98%, 97%, 81%, and 79%, respectively.

Similarly, for the same concentration and for the 45 ^{o}C temperature, cubic and logarithmic models had the highest (95%) value. These models were followed by the quadratic model with 90%. The lowest estimation was made by linear and logistic models with 64% R-square values.

Estimation of the cubic model was the best (97%) for 100 ppm concentration and 25 °C temperature. This was followed by logarithmic (95%), quadratic (89%) and logistic (67%) models. The lowest (65%) estimation had the linear model.

On the other hand, for the same concentration, cubic model provided the highest R-square value (99%) at 35 °C. This model was followed by logarithmic and quadratic models with 95% R-square values. The lowest estimation was made by logistic model with 74% and linear model with 69% R^2 value.

For the same concentration and 45 °C temperature, cubic model had the highest predictive value with 98% R-square value. R-square values for logarithmic, quadratic, logistic and linear models were found 96%, 93%, 78%, and 68%, respectively.

Table 3. Model summary and parameter estimation

	50 ppm	R^2	Constant	b1	b2	b3
25ºC	Linear	.74**	15.27**	.13**		
	Logarithmic	.94**	-4.46*	7.42**		
	Quadratic	.97**	9.25**	.36**	-.00**	
	Cubic	.98**	7.35**	.50**	-.00**	7.11E-006*
	Logistic	.69**	.06**	.99**		
35ºC	Linear	.79**	16.75**	.19**		
	Logarithmic	.95**	-11.03**	10.61**		
	Quadratic	.98**	9.00**	.50**	-.00**	
	Cubic	.98**	7.51**	.61**	-.00**	5.77E-006
	Logistic	.74**	.05**	.99**		
45ºC	Linear	.73**	20.53**	.19**		
	Logarithmic	.97**	-9.20**	11.10**		
	Quadratic	.96**	11.58**	.54**	-.00**	
	Cubic	.98**	7.72**	.82**	-.01**	1.49E-005**
	Logistic	.66**	.04**	.99**		
	75 ppm	R^2	**Constant**	**b1**	**b2**	**b3**
25ºC	Linear	.74**	25.48**	.22**		
	Logarithmic	.97**	-8.15**	12.58**		
	Quadratic	.95**	15.91**	.59**	-.00**	
	Cubic	.98**	11.03**	.94**	-.01**	1.83E-005**
	Logistic	.70**	.03**	.99**		
35ºC	Linear	.81**	29.38**	.27**		
	Logarithmic	.97**	-10.01**	15.07**		
	Quadratic	.98**	19.02**	.68**	-.00**	
	Cubic	.99**	16.87**	.84**	-.01**	8.26E-006
	Logistic	.79**	.02**	.99**		
45ºC	Linear	.64**	43.05**	.20**		
	Logarithmic	.95**	9.55**	12.22**		
	Quadratic	.90**	32.61**	.61**	-.00**	
	Cubic	.95**	25.95**	1.09**	-.01**	2.57E-005**
	Logistic	.64**	.01**	.99**		
	100 ppm	R^2	**Constant**	**b1**	**b2**	**b3**
25ºC	Linear	.65**	45.52**	.25**		
	Logarithmic	.95**	3.93	15.16**		
	Quadratic	.89**	32.81**	.74**	-.00**	
	Cubic	.97**	23.05**	1.44**	-.01**	3.65E-005**
	Logistic	.67**	.01**	.99**		
35ºC	Linear	.69**	43.61**	.34**		
	Logarithmic	.95**	-11.38*	20.34**		
	Quadratic	.95**	25.81**	1.04**	-.00**	
	Cubic	.99**	16.38**	1.72**	-.01**	3.64E-005**
	Logistic	.74**	.01**	.98**		
45ºC	Linear	.68**	45.62**	.37**		
	Logarithmic	.96**	-14.43**	22.15**		
	Quadratic	.93**	27.03**	1.10**	-.00**	
	Cubic	.98**	16.39**	1.87**	-.02**	4.10E-005**
	Logistic	.78**	.01**	.98**		

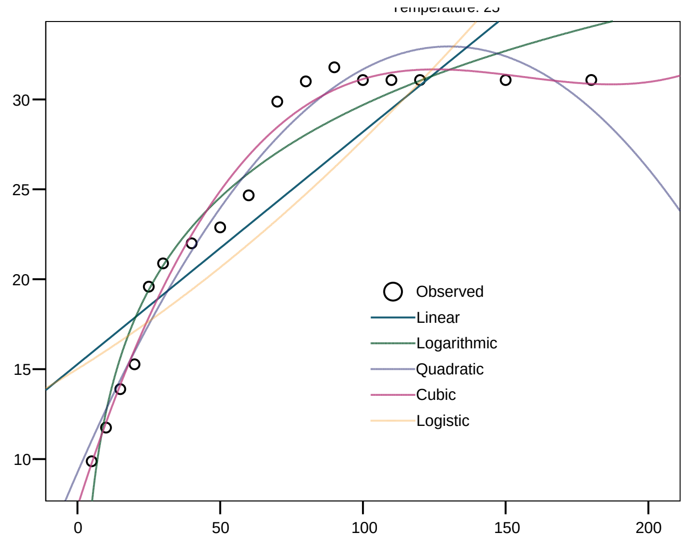

Figure 1. Co 50 ppm 25 °C

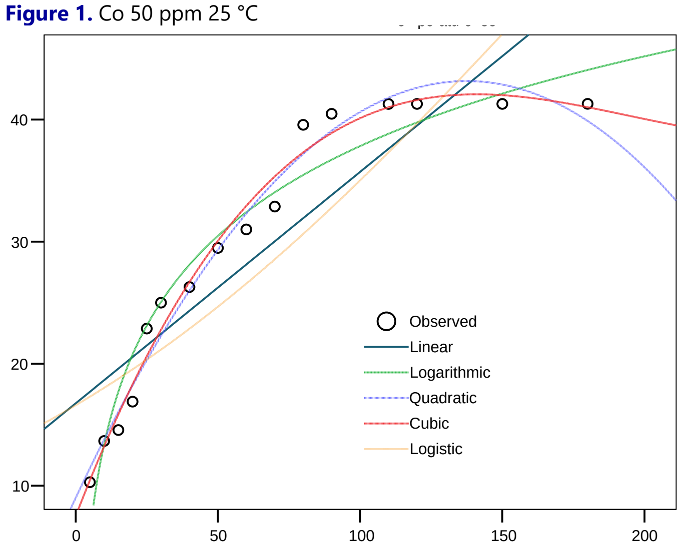

Figure 2. Co 50 ppm 35 °C

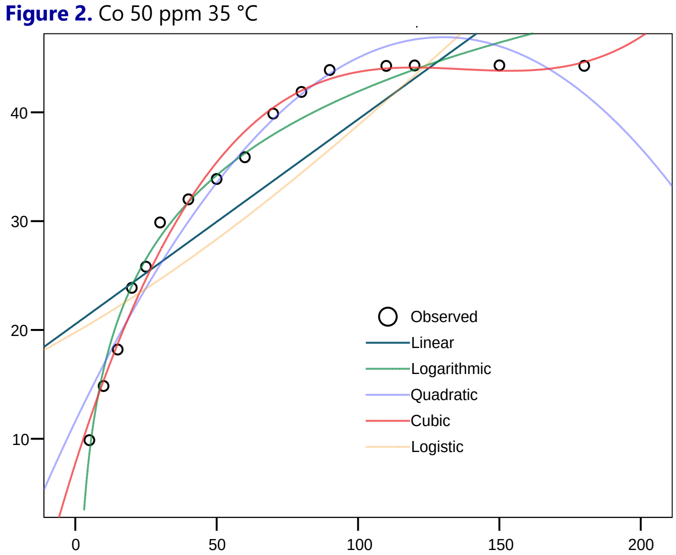

Figure 3. Co 50 ppm 45 °C

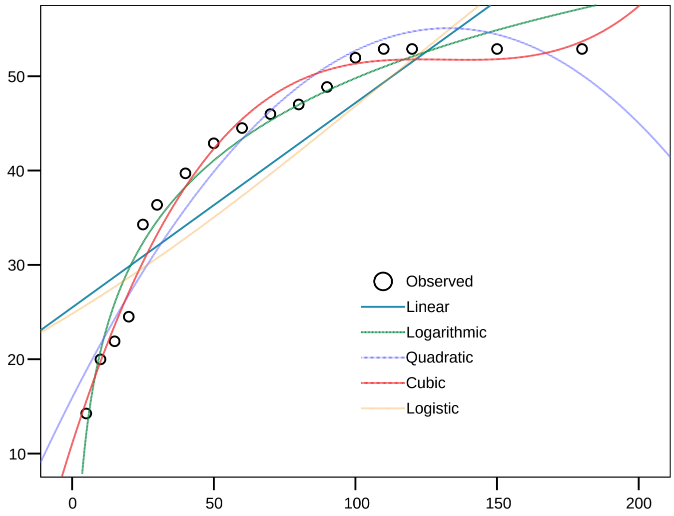

Figure 4. Co 75 ppm 25 °C

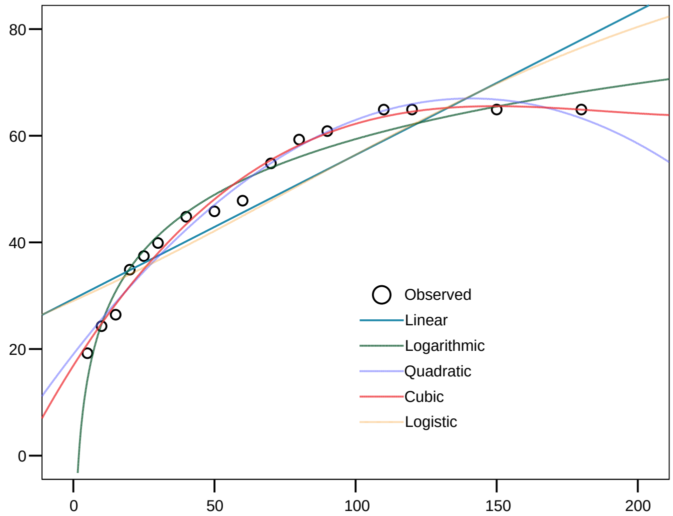

Figure 5. Co 75 ppm 35 °C

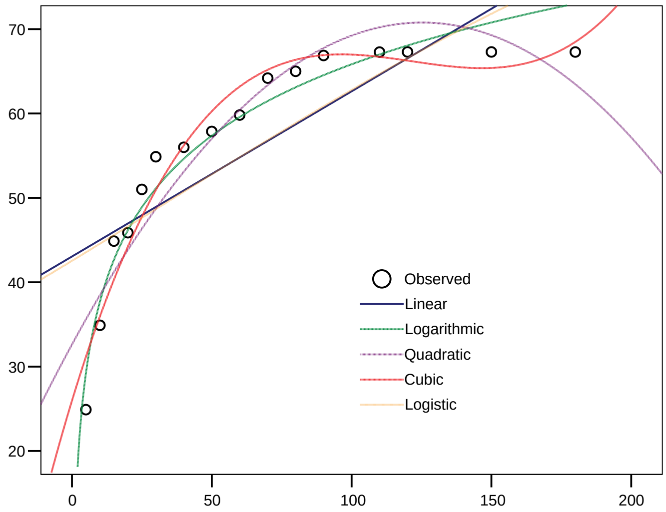

Figure 6. Co 75 ppm 45 °C

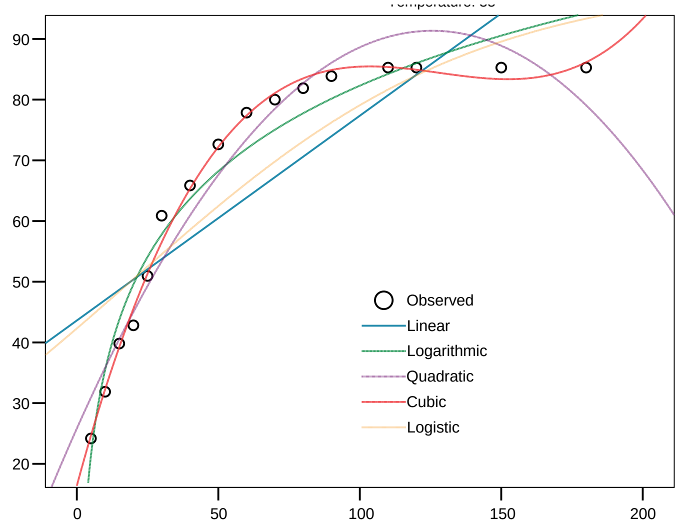

Figure 7. Co 100 ppm 25 °C

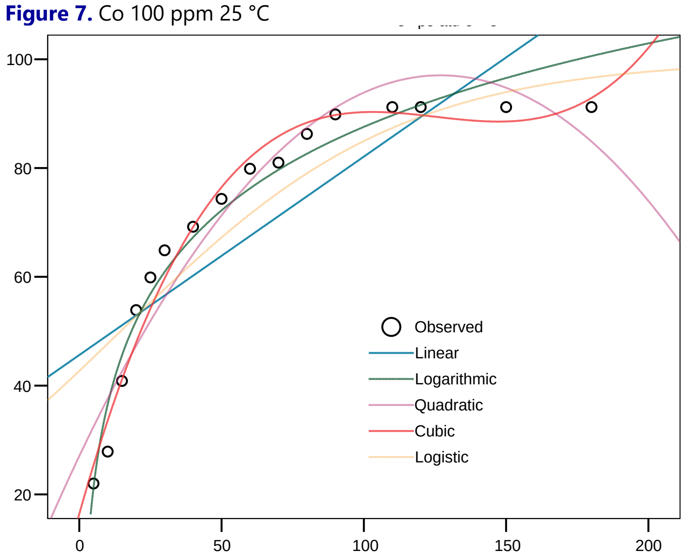

Figure 8. Co 100 ppm 35 °C

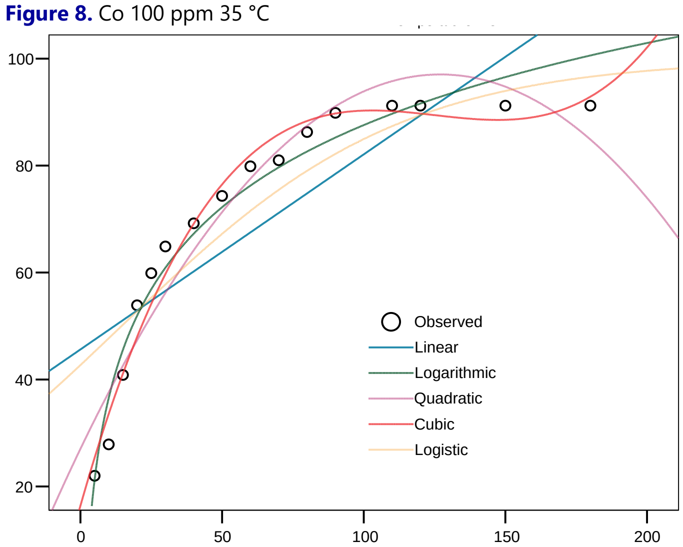

Figure 9. Co 100 ppm 45 °C

DISCUSSION AND CONCLUSIONS

In this study, the adsorption of cobalt ions on Van pumice were examined at various temperatures (25 °C, 35 °C, 45 °C), time (5, 10, 15, ..., 180 min) and (50 ppm, 75 ppm, 100 ppm) concentrations.

By increasing of heavy metal concentration in the solution, the amount of ions increased. Similarly, increasing of contact time the heavy metal ions concentration with Van pumice, it was observed that adsorption was also increased. Adsorption increased directly by proportional mixing time and this increase was fast in the first minutes, and then this stabilized quickly. Similar results have reported [7, 8, 9, 10, 11, 12]. Adsorption efficiency changed with heavy metal ions concentration and the mixing time however, not change with the temperature. In this study, the models having the highest coefficient of determination (R^2) and lowest standard error was indicated the most appropriate models.

Both for all temperature values (25 °C, 35 °C, 45 °C) and for all concentrations (50 ppm, 75 ppm, 100 ppm), cubic model provided the best estimation of the R^2 value which ranges from 95% to 99%. This model was followed by logarithmic model which varies from 94% to 98% R^2 value.

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