OPEN ACCESS
Eurasian Journal of Analytical Chemistry
ISSN: 1306-3057
2017 12(6):913-921
DOI: 10.12973/ejac.2017.00221a

Statistical Modeling of Copper Adsorption on Van Pumice

Canan Demir
Yuzuncu Yıl University, TURKEY
Sıddık Keskin
Yuzuncu Yıl University, TURKEY
Alı Rıza Kul
Yuzuncu Yıl University, TURKEY
Salih Alkan
Ordu University, TURKEY

Received 19 June 2016 ▪ Revised 1 June 2017 ▪ Accepted 3 June 2017

ABSTRACT
Copper (Cu) is an element which is essential for the living. In addition, copper is also one of the first metals used by humans and occurs naturally in nature. The aim of this study is to statistical modeling of copper adsorption on Van Pumice. Van Pumice was used for determination of copper Adsorption level. Modeling, depending on time, was performed to determine for copper 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 cooper 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. Copper concentration and amount of ions have been increased in the solution. In addition, Copper ions adsorption level increased with extending of contacting duration by Van Pumice In addition, adsorption also increased linearly with mixing duration and this increase was ready in the first minutes and then stabilized. The performance of all models to determine the amount of adsorption of copper has been significantly found. However, model the best performance has been shown with the cubic.
Keywords: Cu, adsorption, logarithmic, logistic modeling

INTRODUCTION

The most important industrial activity that effect on spreading of heavy metals are cement production, iron and steel industry, thermal powers, glass production, waste and sludge incinerators. Metal species emitted from the basic industry are different types and amounts in

Correspondence: Canan Demir, *Yuzuncu Yıl University, Vocational School of Health Care, Van, Turkey. Phone: +904322251026/22266.*
canantasin@gmail.com

each industry. Heavy metals released into the air are inhaled by animals and humans. In addition, the part of that reaching to the land is also taken by the plants and the food chain. Heavy metals are effective on animals and humans through the pollination of polluted particles with heavy metals or mixing of industrial waste water into drinking water [1]. Copper (Cu) is an element which is essential for life [2]. Also, copper is one of the first metals that used by humans and is found naturally in nature. Although there are more than 200 copper mineral in nature, only 20 of them have industrial importance [3, 4]. High copper levels were indirectly associated with various neurological disorders such as Alzheimer's and prion diseases [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 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. 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 adsorbe 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 [7, 8, 5]. 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 copper 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 (Cu) in 50 ppm, 75 ppm and 100 ppm concentrations and at pH 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, 110, 120, 150, 180 min). Cu adsorption in Van Pumice example was examined by depending on concentration, temperature and time at pH 5. As mentioned by [9], all adsorption measurements were performed by Thermo Scientific brand the 300 Series II models to a spectrometer [10]. Then of spectrophotometric copper (ppm) was determined indirectly by measuring the copper solutions.

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-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 copper 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 copper ion shaken for 5 minutes, average adsorption amount was 9.45 in 50 ppm concentration however, average concentration was 43.34 when it shaken for 180 minutes in the same concentration. Similarly, at 75 ppm, when shaken for 5 min, the average was 12.70, while it was found 67.00 by increasing of shaking duration to 180 minutes in the same concentration. When copper ions concentration was 100 ppm, adsorbed amount of the substance was 20.75 for 5 min shaking duration, however, this value reached to 89.59 for 180 min shaking duration. By depending on the temperature and concentrations (75 ppm, 100 ppm, 125 ppm), descriptive statistics of adsorbed copper 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 copper ions in different concentrations.

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

	Time	N	Mean (ppm)	S.D. (ppm)	Min (ppm)	Max (ppm)	p
ppm .50	5	3	9,45 ı	0,85	8,47	10,00	0,001
	10	3	12,37 hı	0,50	11,87	12,87	
	15	3	15,01 h	0,24	14,87	15,29	
	20	3	19,21 g	1,17	17,86	19,89	
	25	3	23,82 f	2,48	21,00	25,65	
	30	3	26,56 f	4,22	21,81	29,88	
	40	3	29,95 e	0,34	29,67	30,33	
	50	3	31,34 e	0,49	30,89	31,87	
	60	3	35,35 d	0,85	34,81	36,33	
	70	3	37,65 cd	0,89	37,00	38,66	
	80	3	39,65 bc	0,34	39,31	39,99	
	90	3	40,15abc	0,23	40,00	40,42	
	100	2	41,33 ab	1,89	40,00	42,67	
	110	3	43,17 a	2,28	41,00	45,56	
	120	3	43,34 a	2,40	41,13	45,90	
	150	3	43,38 a	2,46	41,13	46,00	
	180	3	43,34 a	2,46	41,13	45,99	
ppm .75	5	3	12,70k	2,46	9,86	14,33	0,001
	10	3	19,37j	2,20	17,87	21,90	
	15	3	33,33i	2,38	30,58	34,87	
	20	3	38,94ı	2,18	36,87	41,21	
	25	3	42,13h	2,63	39,20	44,31	
	30	3	47,66g	1,61	46,67	49,52	
	40	3	54,50f	,60	53,81	54,88	
	50	3	56,70ef	1,01	55,81	57,81	
	60	3	59,41de	2,73	56,27	61,29	
	70	3	61,42cd	1,86	59,36	63,00	
	80	3	61,99bcd	1,60	60,21	63,29	
	90	3	63,83abc	1,35	62,28	64,80	
	100	2	65,02a	2,32	63,38	66,66	
	110	3	66,88a	1,03	65,97	68,00	
	120	3	67,00a	1,00	66,00	68,00	
	150	3	67,00a	1,00	66,00	68,01	
	180	3	67,00a	1,00	66,00	68,01	
ppm .100	5	3	20,75i	2,72	19,17	23,89	0,001
	10	3	34,34ı	4,81	29,29	38,87	
	15	3	40,16ı	1,48	39,22	41,86	
	20	3	53,82h	5,12	48,40	58,59	
	25	3	62,59g	3,41	59,59	66,29	
	30	3	67,64fg	4,74	62,82	72,31	
	40	3	71,86ef	5,59	66,30	77,49	
	50	3	76,48de	4,88	70,88	79,89	
	60	3	80,60cd	3,69	77,37	84,62	
	70	3	82,59bcd	2,93	79,78	85,63	
	80	3	84,22abc	2,98	81,36	87,30	
	90	3	84,91abc	2,81	82,30	87,89	
	100	2	87,85ab	3,08	85,67	90,03	
	110	3	89,53a	2,25	87,59	92,00	
	120	3	89,61a	2,20	87,67	92,00	
	150	3	89,59a	2,23	87,59	92,00	
	180	3	89,59a	2,23	87,60	92,00	

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

	°C	N	Mean	Sd	Min.	Max.	p
ppm.50	25	17	30,30	11,37	10,00	41,13	0,86
	35	16	31,00	11,68	9,87	43,00	
	45	17	32,52	12,44	8,47	46,00	
ppm.75	25	17	51,64	16,34	13,90	66,00	0,96
	35	16	50,97	18,17	9,86	67,00	
	45	17	52,72	17,42	14,33	68,01	
ppm.100	25	17	70,94	20,01	23,89	87,67	0,93
	35	16	71,86	22,44	19,18	89,17	
	45	17	69,10	23,15	19,17	92,00	

In order to determine the adsorption of copper ions on Van pumice, results of the used models are given in **Table 3**. As seen **Table 3**, Cubic model with 99% R^2 value was the best model for 50 ppm and 25 °C temperature. This model was followed by quadratic model with 98%, logarithmic model with 95% and linear model with 76% R^2 values. The logistic model was the last with 71%. Cubic model was also the best model with 99% R^2 value at 35 °C. This model was followed by quadratic model with 97%, logarithmic model with 96% and linear model with 75% R^2 value. The logistic model was included in last with 68%. When temperature was 45 °C, the best estimations were made by Cubic and logarithmic models with 98% R^2 value. These models were followed by quadratic model with 96% and linear model with 85% R^2 value. The lowest estimation was made by logistic models with 76% R^2 value.

When we look at the table values to 75 ppm and 25 ° C temperature, cubic and logarithmic models were the best models with 94% R-square value. This was followed by quadratic model with 87%, linear model with 64% and logistic model with 60%. For the same concentration and 35 °C temperature, Cubic model had the highest predictive value with 99% R-square value. R-square values for logarithmic, quadratic, logistic and linear models were found 96%, 92%, 65%, and 60%, respectively. Similarly, for the same concentration and for the 45 ^{o}C temperature, cubic model had the highest (98%) value. This model was followed by the logarithmic model with 97%, quadratic model with 93%, logistic model with 74% and linear model with 70% R-square value. Estimation of the cubic model was the best (98%) for 100 ppm concentration and 25° C temperature. This was followed by logarithmic (95%), quadratic

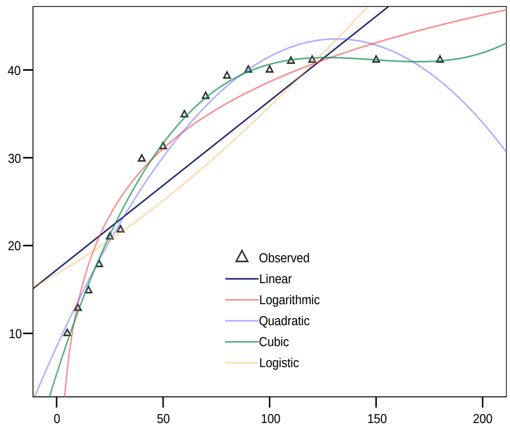
(90%) and logistic (72%) models. The lowest (64%) estimation had the linear model. On the other hand, for the same concentration, cubic model provided the highest R-square value (96%) at 35 °C. R-square values of logarithmic, quadratic, logistic and linear models were found 91%, 86%, 64% and 56%, respectively. For the same concentration and 45 ^{o}C, unlike other concentration and temperature, logarithmic model was the best model with 99% R-square value. This was followed by the cubic (98%), quadratic (95%) and, logistic (89%) and linear (80%) models.

Table 3. Model Summary and parameter estimators

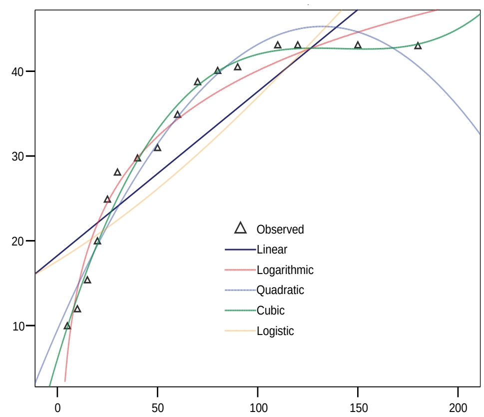
	50 ppm	R^2	Constant	b1	b2	b3
25 °C	Linear	0,76**	17,22**	0,19**		
	Logarithmic	0,95**	-11,88**	10,98**		
	Quadratic	0,98**	8,49**	0,53**	-0,00**	
	Cubic	0,99**	5,36**	0,76**	-0,01**	1,17E-005**
	Logistic	0,71**	0,05**	0,99**		
35 °C	Linear	0,75**	18,25**	0,19**		
	Logarithmic	0,96**	-11,56**	11,21**		
	Quadratic	0,97**	9,47**	0,54**	-0,00**	
	Cubic	0,99**	6,03**	0,79**	-0,01**	1,33E-005**
	Logistic	0,68**	0,05**	0,99**		
45 °C	Linear	0,85**	15,89**	0,26**		
	Logarithmic	0,98**	-15,12**	12,44**		
	Quadratic	0,96**	8,70**	0,59**	-0,00**	
	Cubic	0,98**	5,05*	0,88**	-0,01**	2,08E-005*
	Logistic	0,76**	0,05**	0,99**		

	75 ppm	R^2	Constant	b1	b2	b3
25 °C	Linear	0,64**	34,32**	0,26**		
	Logarithmic	0,94**	-8,73*	15,70**		
	Quadratic	0,87**	21,60**	0,75**	-0,00**	
	Cubic	0,94**	11,70**	1,46**	-0,01**	3,71E-005**
	Logistic	0,60**	0,02**	0,99**		
35 °C	Linear	0,65**	32,55**	0,28**		
	Logarithmic	0,96**	-15,00**	17,38**		
	Quadratic	0,92**	17,25**	0,89**	-0,00**	
	Cubic	0,99**	7,26**	1,61**	-0,01**	3,85E-005**
	Logistic	0,60**	0,02**	0,99**		
45 °C	Linear	0,74**	30,91**	0,34**		
	Logarithmic	0,97**	-14,45**	17,61**		
	Quadratic	0,93**	17,44**	0,96**	-0,00**	
	Cubic	0,98**	8,06**	1,71**	-0,02**	5,34E-005**
	Logistic	0,70**	0,02**	0,99**		

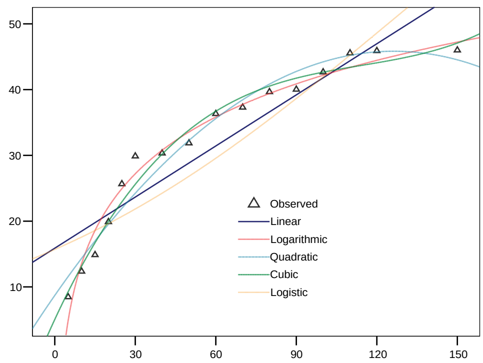
	100 ppm	R^2	Constant	b1	b2	b3
25 °C	Linear	0,64**	49,77**	0,31**		
	Logarithmic	0,95**	-3,23	19,29**		
	Quadratic	0,90**	33,14**	0,96**	-0,00**	
	Cubic	0,98**	20,82**	1,84**	-0,02**	4,61E-005**
	Logistic	0,72**	0,01**	0,98**		
35 °C	Linear	0,56**	50,76**	0,32**		
	Logarithmic	0,91**	-7,45	20,89**		
	Quadratic	0,86**	31,04**	1,10**	-0,01**	
	Cubic	0,96**	15,31**	2,24**	-0,02**	6,07E-005**
	Logistic	0,64**	0,01**	0,98**		
45 °C	Linear	0,80**	38,95**	0,47**		
	Logarithmic	0,99**	-20,42**	23,42**		
	Quadratic	0,95**	23,60**	1,17**	-0,01**	
	Cubic	0,98**	14,16**	1,93**	-0,02**	5,37E-005**



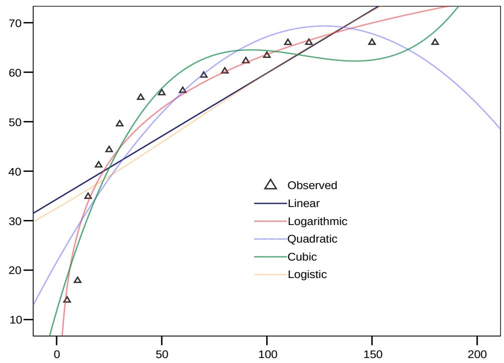
Cu 50ppm 25°C



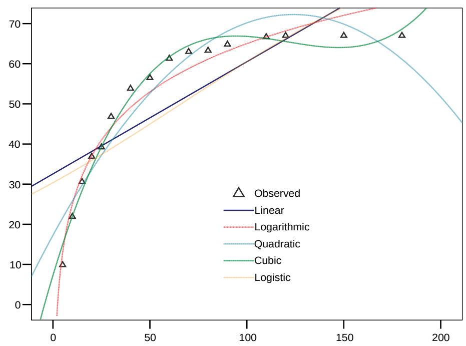
Cu 50ppm 35°C



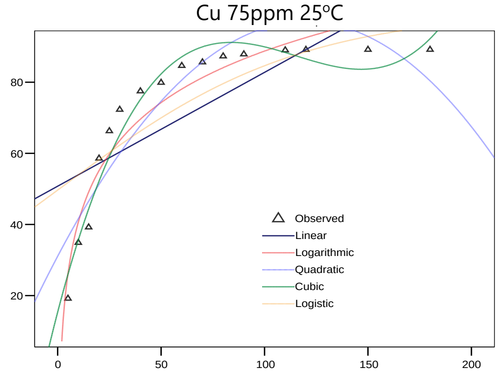
Cu 50ppm 45°C



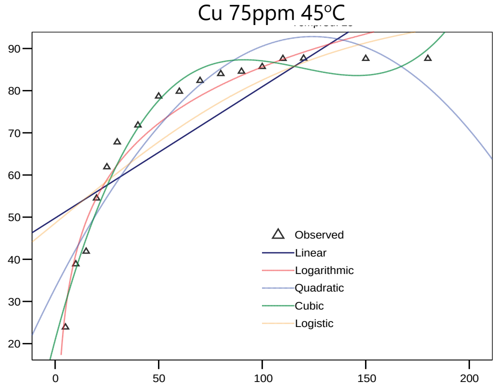
Cu 75ppm 25°C



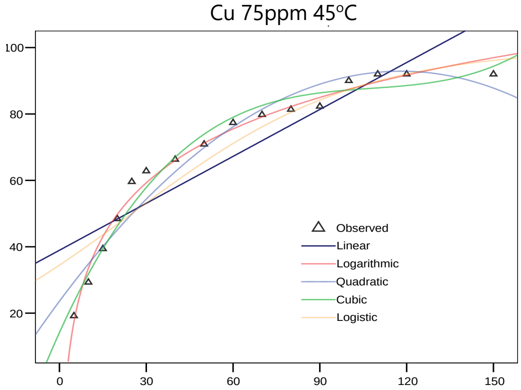
Cu 75ppm 45°C



Cu 75ppm 45°C



Cu 100ppm 25C



Cu 100ppm 45C

DISCUSSION AND CONCLUSIONS

In this study, the adsorption of copper 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 was also increased. Similarly, increasing of contact time the heavy metal ions concentration with Van pumice, it was observed that adsorption was overwhelmingly increased. 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 Koyuncu et al., (2005); Çalışkan et al., (2005); Çokadar et al., (2003); Abollino et al., (2003); Akyüz et al., (2001); and Kul (1999) [11, 12, 13, 14, 15, 16]. 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 (50ppm, 75ppm, 100ppm), cubic model provided the best estimation of the R^2value which ranges from 96% to 99%. This model was followed by logarithmic model which varies from 91% to 99% R^2 value.

REFERENCES

1. Kahvecioğlu, Ö., Kartal, G., Güven, A., & Timur, S., (2003). Metallerin Çevresel Etkileri. *Tmmob Metalurji Mühendisleri Odası Dergisi, 136*, 47-53.
2. Stern, B. R., Solioz, M., Krewski, D., Aggett, P., Aw, T. C., Baker, S., Crump, K., Dourson, M., Haber, L., Hertzberg, R., Keen, C., Meek, B., Rudenko, L., Schoeny, R., Slob, W., & Starr, T. (2007). Copper and Human Health: Biochemistry, Genetics, and Strategies for Modeling Dose-response Relationships. *J of Toxicol and Environ Health B Crit Rev., 10*(3), 157-222.
3. Şener, Ş. (2010). Ağır Metallerin Çevresel Etkileri. *SDUGEO (Online: www.geo.sdu.edu.tr), e-dergisi (Süleyman Demirel Üniversitesi Jeoloji Mühendisliği), 1*(3), 33-36, ISSN 1309-6656.
4. Alacabey, İ. Doğal ve Aktive Edilmiş Van Gölü Sediment (Dip Çamuru) Örneklerinin Bazı Ağır Metallerle Adsorspsiyonunun İzoterm ve Termodinamik Analizi (doktora tezi). Yüzüncü Yıl Üniversitesi, Fen Bilimleri Enstitüsü, Doktora Tezi, Van.
5. Çiçek, H. (2005). Atık Sulardan Fenolün Giderilmesinde Şeker Pancarı Küspesinden Elde Edilen Aktif Karbonun Kullanılması (Yüksek Lisans Tezi). Fırat Ü., Fen Bil. Ens., Elazığ, pp. 114.
6. Tekir, O. (2006). Fındık Zürufundan Aktif Karbon Eldesi Ve Bazı Ağır Metallerin İyonlarının Adsorpsiyonu (Yüksek Lisans Tezi). Sakarya Üniversitesi, Fen Bilimleri Enstitüsü, Sakarya.
7. Berkem, A.R., & Baykut, S. (1980). Fizikokimya, İstanbul Üniversitesi Yayınları, No: 42, İstanbul. pp. 1111.
8. Sarıkaya, Y., (1993). Fizikokimya, Gazi Kitapevi, Ankara, s.633-653.
9. Küçükgül, E. Y., & Kutlu, S. (2006). Çinko ve bakırın sulu çözeltide aktif karbonla tekli adsorbsiyonu. *DEÜ Mühendislik Fakültesi Fen ve Mühendislik Dergisi, 8*(2), 21-30
10. Benek, V. (2015). Van Bölgesindeki Doğal Pomza Taşının Bazı Ağır Metallerin Adsorpsiyonunda Kullanılması (Yüksek Lisans Tezi). Yüzüncü Yıl Üniversitesi, Fen Bilimleri Enstitüsü, Yüksek Lisans Tezi, Van.
11. Koyuncu, H., Kul, A., Ceylan, H., Yıldız, N., & Çalımlı, A. (2005). 3-Hidroksibenzaldehitin Doğal ve Aktive Edilmiş Bentonit Üzerindeki Adsorpsiyon Denge Çalışmaları. 12. Ulusal Kil Sempozyumu Bildirileri. 05-09 Eylül 2005, Van. 243-244.

12. Çalışkan, E. (2005). Asi Nehri'nde Su, Sediment ve Karabalık (Clarias gariepinus burchell, 1822)'ta Agır Metal Birikiminin Araştırılması (yüksek lisans tezi). *Mustafa Kemal Üniversitesi, Fen Bilimleri Enstitüsü, Hatay*.
13. Çokadar, H., İleri R., Ateş, A., & İzgi B. (2003). Nikel(II) iyonunun sulu ortamdaki granül aktif karbon (GAK) ile giderilmesi. *Çev-Kor Dergisi, 12*(46), 38-42.
14. Abollino, O., Aceto, M., Malandrino, M., Sarzanini, C., & Mentasti, E. (2003). Adsorption of heavy metals on Na-montmorillonite. Effect of pH and organic substances. *Water Research, 37*(7), 1619-1627.
15. Akyüz, S., Akyüz, T., & Ozer N. M. (2001). FT-IR spectroscopic investigations of benzidine and bipyridyls adsorbed on diatomite form Anatolia. *Journal of Molecular Structure, 565-566*, 493-496.
16. Kul, A. R. (1999). Çözelti ortamında bulunan bazı organik maddelerin ticari aktif karbonlar üzerindeki adsorpsiyonlarının incelenmesi, (doktora tezi). *Yüzüncü Yıl Üniversitesi, Fen Bilimleri Enstitüsü, Doktora Tezi, Van*.