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Adsorption Kinetics of Cu(II) and Ni(II) Ions Using Clay in Kulp District of Diyarbakır Province

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Keywords

Adsorption

Copper

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Temparature

Abstract

In this study, the adsorption kinetics of Cu(II) and Ni(II) ions in the aqueous medium of the natural clay sample found in Kulp district of Diyarbakır province were investigated. For this purpose, the characterization of the natural clay mineral found in Kulp district of Diyarbakır province was carried out using X-Ray (XRD and XRF) and BET methods. The copper and nickel from the aqueous medium was measurmented at 25, 35 and 45 degrees. When the obtained data were applied to other models, it was found that it followed the Ho McKay equation for both ions. The qmax values here were measured as 1.51, 2.05, 2.30 for Cu(II) and 1.044, 1.086 and 1.741 for Ni(II) at the working temperatures, respectively. The increase in qmax values shows the accuracy of our study.

Cite

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1. INTRODUCTION

The development of the industry, increasing the number of heavy metals in the waters, created an important threat to environmental problems (Borst et al., 2020). It is necessary to remove heavy metals in polluted waters before giving them to the ecosystem. For this, many physical and chemical methods have become more popular recently.

The basis of the adsorption process is based on the equilibrium of unbalanced forces as a result of the interaction of molecules or ions in the aqueous medium with the groups on solid surface (Sarı & Tüzen, 2009). Natural adsorbents; clays, natural zeolites, bio sorbents can be given as examples. As an example of artificial adsorbents, activated charcoal and nanomaterials can be modified.

In order to remove cadmium and lead from the aqueous medium, calcalite was used as an absorbent. The measured values were found to be compatible with the Langmuir model. The percentages of removal at room temperature for natural calcite were determined to be approximately 20 mg/g for both metals (Yavuz et al., 2007).

Using palygorskite clay as a natural absorbent, lead, nickel, chrome and copper in river waters in South Africa were removed from the aqueous medium (Potgieter et al., 2006). Kaolinite and montmorillonite were used as adsorbent for iron, cobalt and nickel. Many parameters on metal removal were investigated (Bhattacharyya & Gupta, 2008). Modified Ünye clay was used for copper ions. Absorption capacity was found to be large (Eren, 2008).

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In other studies, natural kaolinite (Jiang et al., 2010), chitosan-clay composite (Tirtom et al., 2012), Nigerian kaolinite clay (Dawodu & Akpomie, 2014), modified Cucurbita moschata (a new adsorbent) (Khan & Rao, 2017), natural Arabian clay (Mu'azu et al., 2020) were used as absorbents and the removal of metal ions was achieved at a high rate.

In this study, natural clay found in Kulp district of Diyarbakır was used as absorbent. The effects of various temperatures and times were investigated to increase the adsorption of Cu(II) and Ni(II) ions to a high level. The analytical parameters of the method were measured. Its performance in removing ions was compared with other natural and modified absorbents in the literature.

2. MATERIAL AND METHOD

Materials

In the experiments, analytical purity Cu $(NO_3)_2$ and Ni $(NO_3)_2$ salts were used. The required amounts were weighed and 1000 mg/L stock solutions were prepared for each. Sortarious brand deionized water was used in the preparation of the solutions.

Clay sample

In this study, clay containing natural talc from Kulp district of Diyarbakir was used as adsorbent. The chemical content of the clay used as an adsorbent in the study; 63.4 % SiO_2, 0.2 % Al_2O_3, 0.2 % CaO, 3.3 Fe_2O_3, 26.4 %MgO, ≤ 1.0 % K_2O, ≤ 0.1 % Na_2O, ≤ 0.8 % TiO_2, ≤ 0.1 P_2O_5, ≤ 0.1 MnO and 5.30 % A.Za determined as a result of XRF analysis methods.

Characterization of clay

Clay sample containing natural talc brought from Kulp district of Diyarbakır was dried at approximately 100 °C. It was broken and ground and passed 150 mm electrified. Then it was dried again at 105 °C and stored in a desiccator to be used in experiments. The structure of the clay samples was determined by taking the XRD spectrum and is shown in Figure 1.

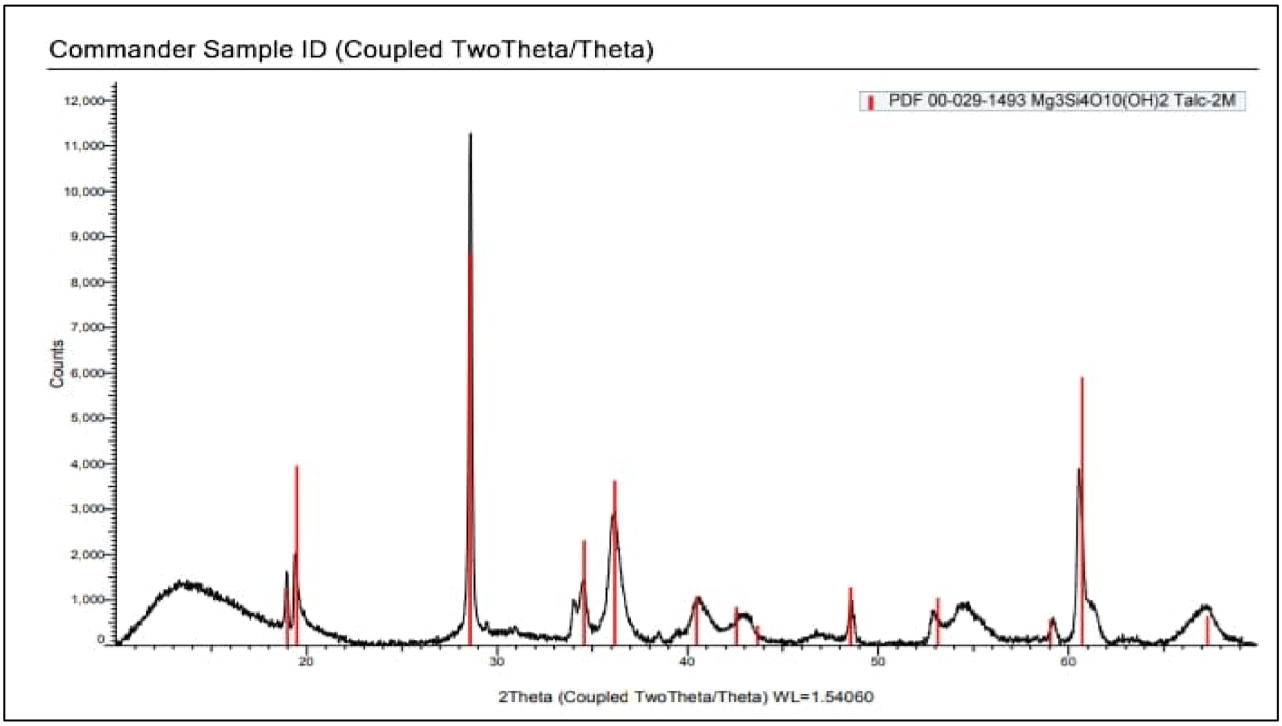

Figure 1. *XRD spectrum of clay*

Analyses of Cu(II) and Ni(II)

Analyses of Cu(II) and Ni(II) in aqueous media were investigated depending on temperature and time. Stock solutions of these two ions were prepared 10 ml each of the solutions containing both ions to be examined were transferred to 100 ml reagent bottles and a certain amount of clay sample was placed. It was shaken for a certain time and at certain temperatures. The clay was then separated using a centrifugation step for 15 minutes. Metal concentrations in solution were measured by atomic absorption spectrometry. Hollow cathode lamps of ions were used in the analysis. Lights with wavelengths of 327.39 and 231.60 nm were selected for the analysis of Cu(II) and Ni(II) ions.

Theory of adsorption

The measured data were applied to other models and the results were compared. The parameter that is effective in the compatibility of the measured values with the models is the correlation coefficient. During operation, the effect of contact time and temperature was examined. Measurements were made when Cu and Ni concentrations were 100 mg l^{-1} and adsorbent amount was 1 g. The adsorption of metal ions depends on the pH of the absorbent medium. The silicon value in the absorbent content determines the working pH value of the environment. Since the clay contains 57% silicon dioxide, the appropriate pH range 6 was used.

Since adsorption is time dependent, it is important to measure the equilibrium contact time in adsorption kinetics. The following models are used to determine the equilibrium contact times.

Lagergren Model: It was the first of the kinetic model. It is done by the Equation (1) given below (Yavuz et al., 2002). An increase in the q value indicates an increase in adsorption.

$$\ln(qm - qt) = \ln qm - k_1 t \tag{1}$$

Ho McKay Model: This model is the kinetic model developed (Ho & Mckay, 1998). The expression showing how the adsorption capacity changes with time is given in Equation (2).

$$\frac{t}{qt} = \frac{1}{K2\,qe^2} + \frac{t}{qe} \tag{2}$$

Elovich Kinetic Model: This model gives information about the adsorption process on the solid surface. This model also took place in the literature as the model developed by Roginsky and Zeldovich and was formulated as Equation (3) (Baytar et al., 2018).

$$qt = \frac{1}{\beta}(\ln \alpha\beta) + \frac{1}{\beta}\ln t \tag{3}$$

Weber-Morris Kinetic Model: This model was preferred to examine the internal particulate diffusion phenomenon. In this model, using the formula in Equation (4), the effect of boundary layer resistance, balance, velocity and contact time from the parameters of solution adsorption is measured (Onursal et al., 2020).

$$qt = k_i\sqrt{t} + C \tag{4}$$

3. RESULTS AND DISCUSSION

Kinetic studies of Cu(II)

In kinetic studies, the contact time and the amount of adsorbed substance are examined. For this purpose, the amount of adsorbed material was measured between 0-140 minutes and at 25, 35 and 45 degress. The data were given in the figures (Dal et al., 2021). When Figure 2 is examined, as the time increases, the amount of adsorbed material decreases and at the same time the temperature decreases. With the increase in the amount of adsorbed substance observed to increase (Fu et al., 2021). Adsorption graphs of Cu(II) according to kinetic models are given as Figures 3, 4, 5 and 6.

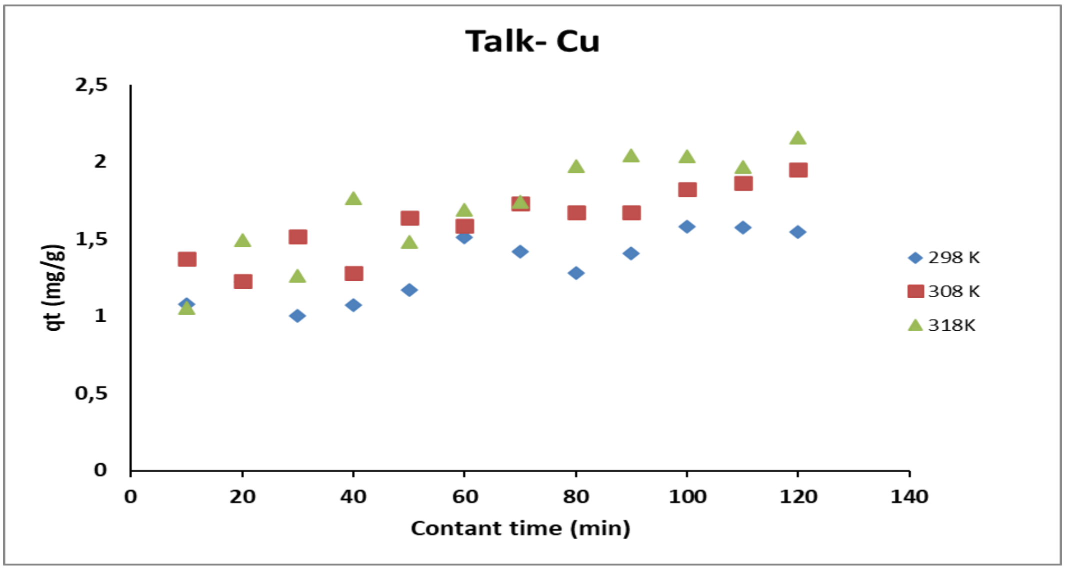

Figure 2. *The contact time on Cu(II) concentration*

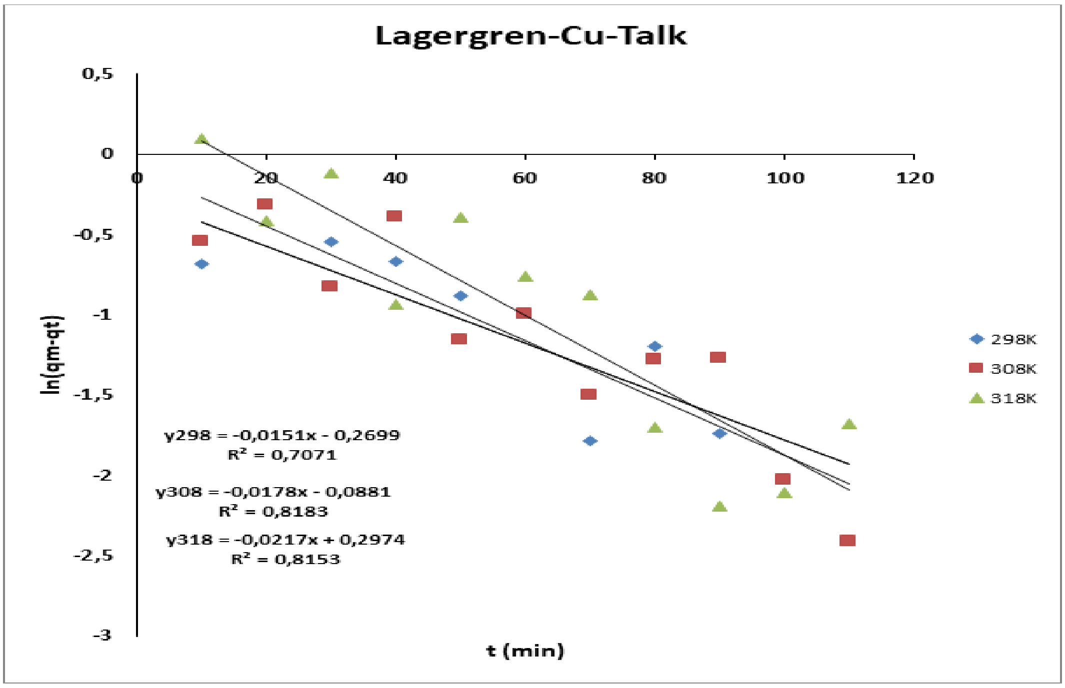

Figure 3. *Lagergren plot of Cu(II) adsorption*

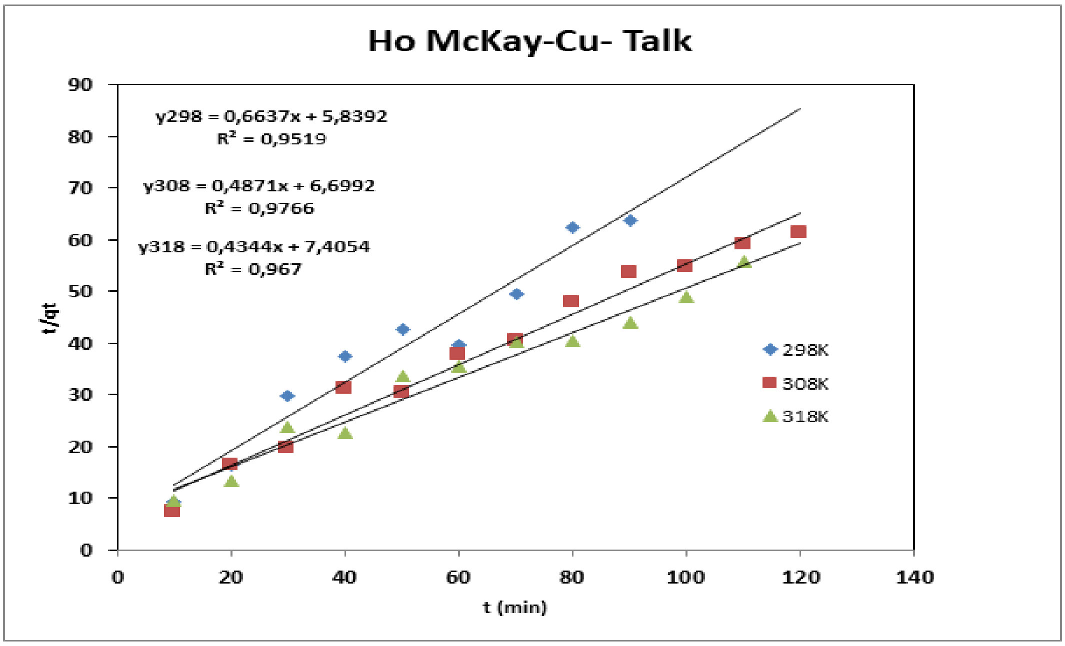

Figure 4. *Ho-Mac Kay plot of Cu(II) adsorption*

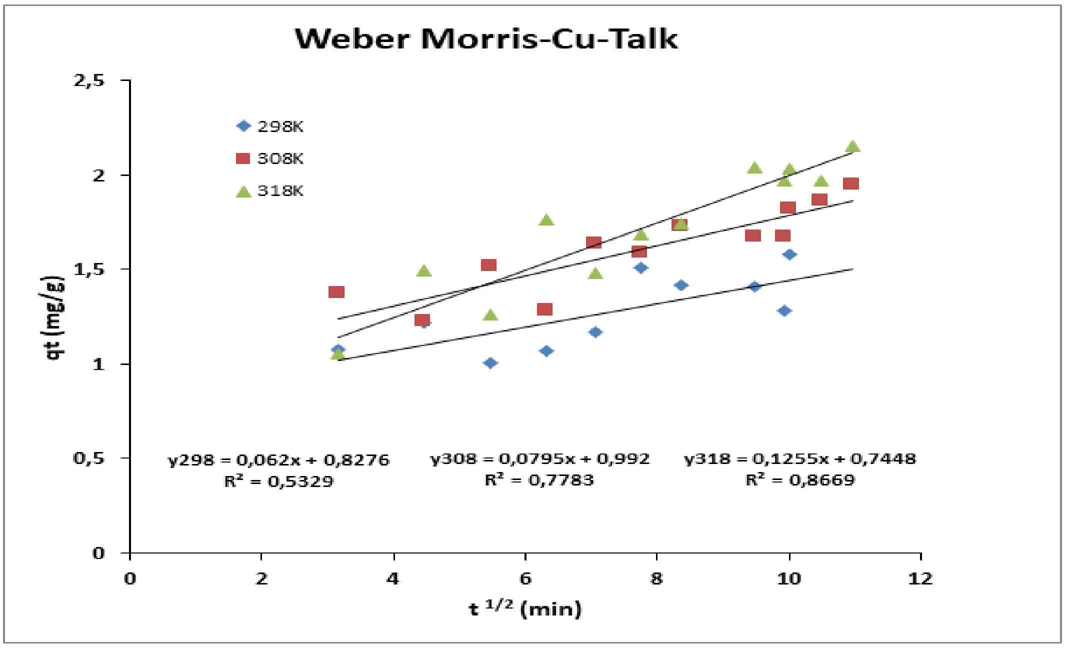

Figure 5. *Weber-Morris plot of Cu(II) adsorption*

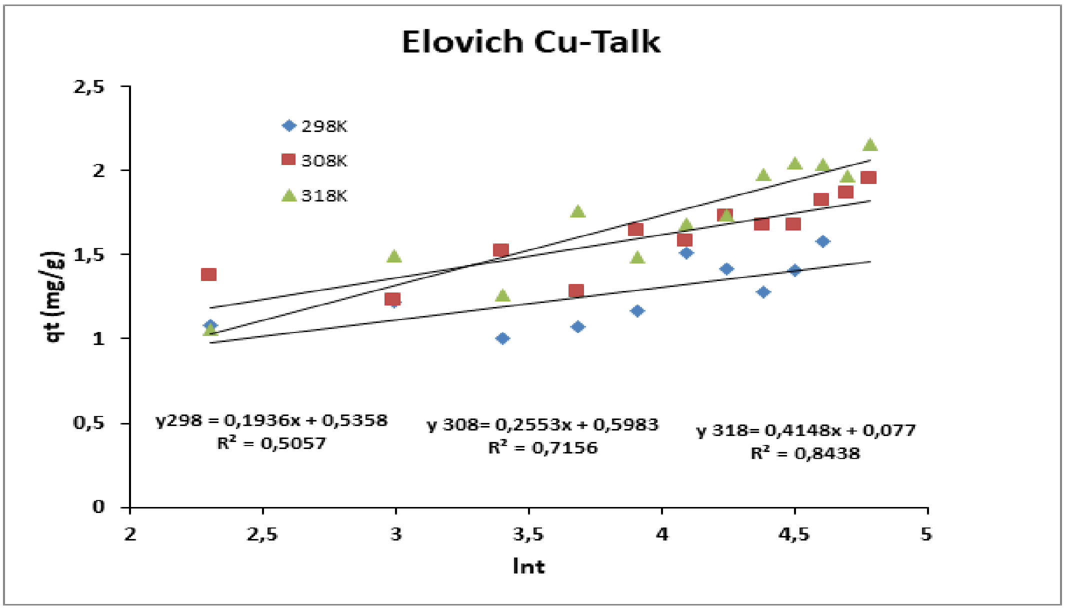

Figure 6. *Elovich plot of Cu adsorption (II)*

Data from models are shown in Table 1.

Table 1. *Parameters according to kinetic velocity models*

Lagergren's Equation $ln(q_e - q_t) = lnq_e - k_1 t$				
(°K)	**Line Equation**	**R^2**	**k_1 = m**	**n = lnq_e**
298	y=-0,0154x-0,4696	0,37	0,0154	0,4696
308	y=-0,0178x-0,0881	0,82	0,0178	-0,0881
318	y=-0,0217x+0,2974	0,81	0,0217	0,2974

Ho McKay's Equation $t/q_t = t/q_e + 1/k_2 q_e^2$				
(°K)	**Line Equation**	**R^2**	**q_e (mg/g)**	**k_2**
298	y=0,6637x+5,8392	0,95	1,51	0,0007
308	y=0,4871x+6,6992	0,98	2,05	0,0239
318	y=0,4344x+7,4054	0,97	2,30	0,0255

Weber-Morris's Equation $q_t = C_b + K_{WM}\sqrt{t}$				
(°K)	**Line Equation**	**R^2**	**K_{WM}**	**C_b**
298	y=0,0662x+0,8276	0,53	0,0662	0,8276
308	y=0,0795x+ 0,9920	0,78	0,0795	0,9920
318	y=0,1255x+0,7448	0,87	0,1255	0,7448

Elovich's Equation $q_t = (1/\beta)\, ln(\alpha\beta) + (1/\beta)\, ln\, t$				
(°K)	**Line Equation**	**R^2**	**β**	**α**
298	y=0,1936x+0,558	0,50	5,1652	3,455
308	y=0,2553x+0,5983	0,71	3,9170	2,659
318	y=0,4148x+0,077	0,84	2,4108	0,499

Kinetic studies of Ni(II)

Adsorption studies of Ni(II) were performed by applying the procedure in Cu(II) (Ewis et al., 2022). First of all, the contact time of Ni(II) at 298K, 308K and 318K was measured within 0-140 seconds and is show in Figure 7.

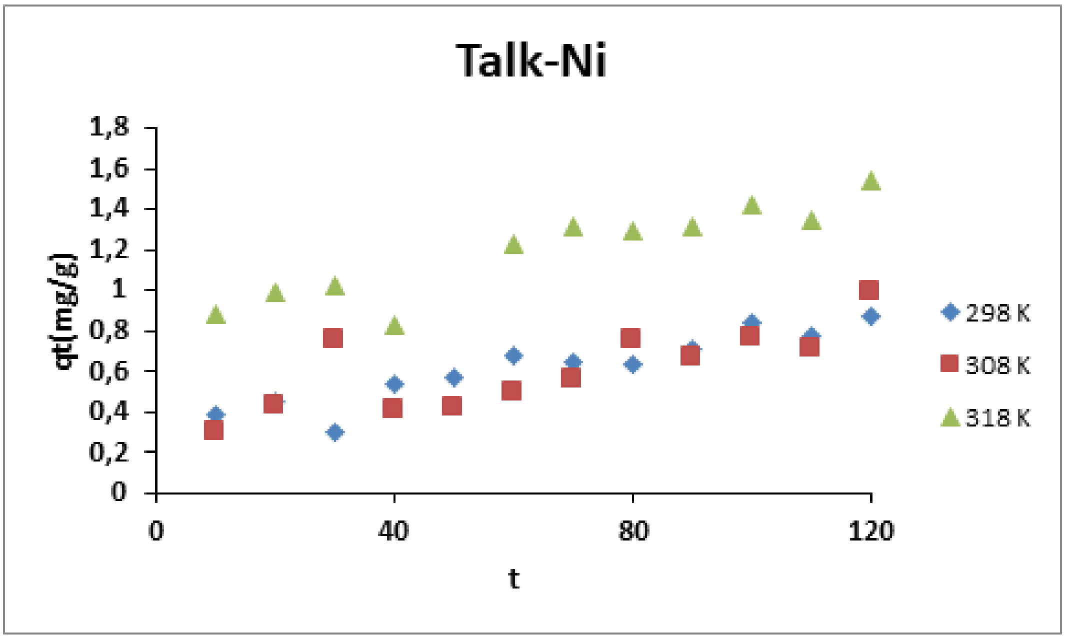

Figure 7. *The contact time on Ni(II) concentration*

Adsorption graphs of Ni(II) according to kinetic models are given as Figures 8, 9, 10 and 11.

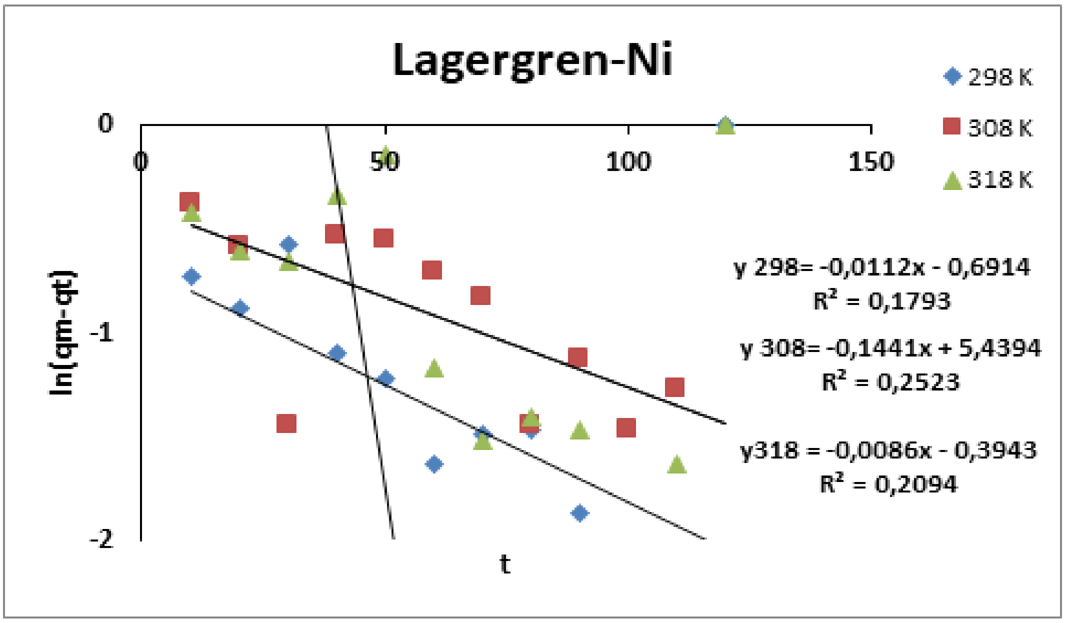

Figure 8. *Lagergren plot of Ni adsorption (II)*

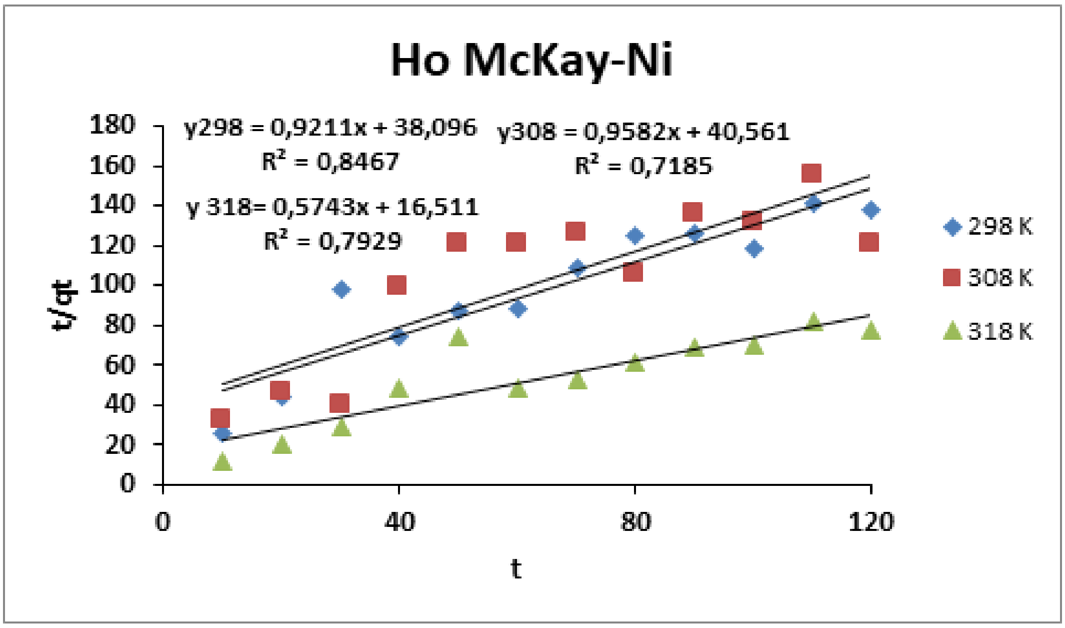

Figure 9. *Ho-Mac Kay plot of Ni(II) adsorption*

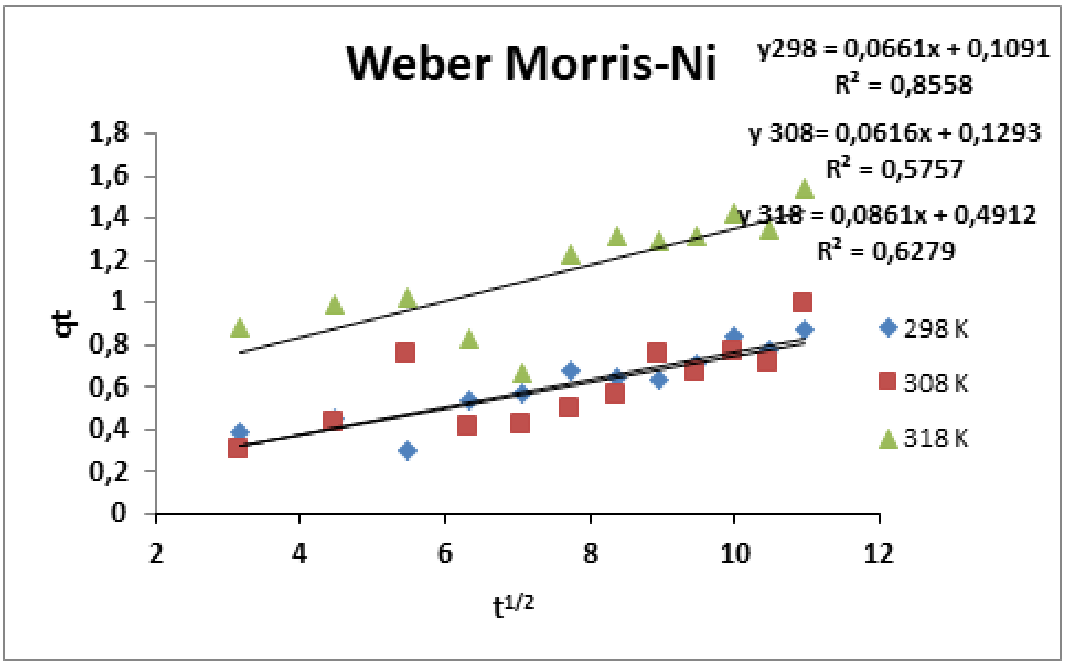

Figure 10. *Weber-Morris plot of Ni(II) adsorption*

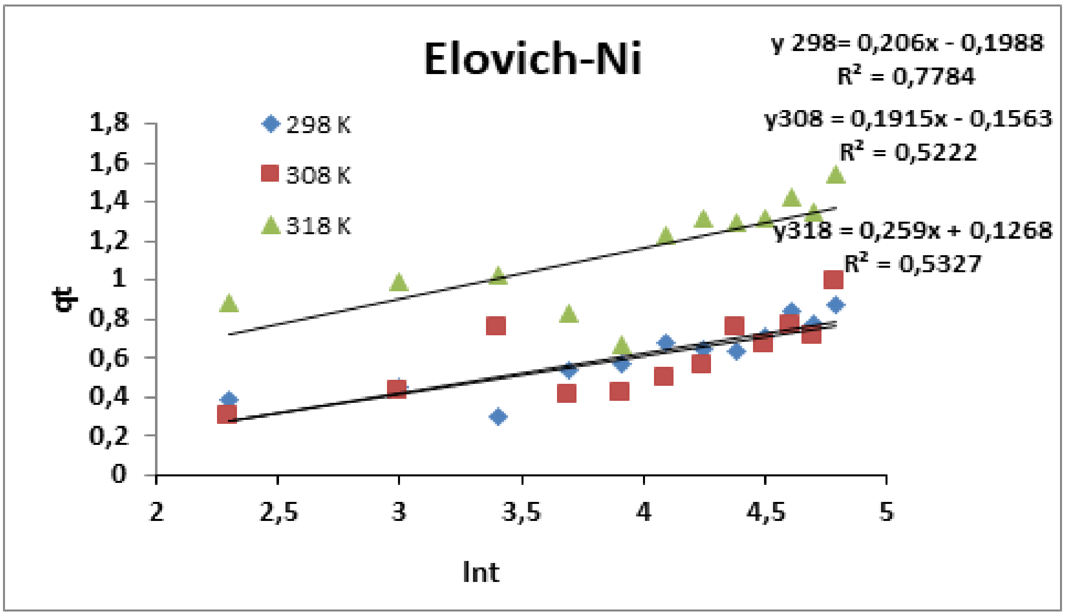

Figure 11. *Elovich plot of Ni(II) adsorption*

Data from models are shown in Table 2.

Table 2. *Parameters according to kinetic velocity models*

Lagergren's Equation $ln(q_e - q_t) = lnq_e - k_1 t$				
(°K)	**Line Equation**	**R^2**	**$k_1 = m$**	**$n = lnq_e$**
298	y=-0,0112X-0,6914	0,18	-0,0112	-0,6914
308	y=-0,1441X+5,4394	0,25	-0,1441	5,4394
318	y=-0,0086X-0,3943	0,21	-0,0086	-0,3943

Ho McKay's Equation $t/q_t = t/q_e + 1/k_2 q_e^2$				
(°K)	**Line Equation**	**R^2**	**q_e (mg/g)**	**k_2**
298	y=0,9211X+38,096	0,85	1,086	0,022
308	y=0,9582X+40,561	0,72	1,044	0,023
318	y=0,5743X+16,511	0,79	1,741	0,019

Weber-Morris's Equation $q_t = C_b + K_{WM}\sqrt{t}$				
(°K)	**Line Equation**	**R^2**	**K_{WM}**	**C_b**
298	y=0,0661X+0,1091	0,85	0,0661	0,1091
308	y=0,0616X+0,1293	0,57	0,0616	0,1293
318	y=0,0861X+0,4912	0,63	0,0861	0,4912

Elovich's Equation $q_t = (1/\beta)\, ln(\alpha\beta) + (1/\beta)\, ln\, t$				
(°K)	**Line Equation**	**R^2**	**β**	**α**
298	y=0,206X-0,1988	0,78	4,854	0,078
308	y=0,1915X-0,1563	0,52	5,222	0,084
318	y=0,259X+0,1268	0,53	3,861	0,422

4. CONCLUSION

In this study, the chemical structure of the clay sample brought from the Kulp district of Diyarbakır was examined using XRD. Using XRF, its chemical structure was determined as 63.4 % SiO_2, 0.2 % Al_2O_3, 0.2 % CaO, 3.3 Fe_2O_3, 26.4 %MgO, ≤ 1.0 % K_2O, ≤ 0.1 % Na_2O, ≤ 0.8 % TiO_2, ≤ 0.1 P_2O_5, ≤ 0.1 MnO and 5.30 % A.Za determined as a result of XRF analysis methods.

This clay sample was also used as an adsorbent in our studies. Both ion samples were shaken with this adsorbent at 298K, 308K and 318K for 0-140 minutes. The adsorption kinetics of the samples were investigated.

The adsorption kinetics of this sample were carried out separately for both Cu(II) ion and Ni(II) ion at different temperatures using Lagergren, Ho-Mac Kay, Weber-Morris and Elovich equations. The qmax values were calculated as 1.51, 2.05 and 2.30 for Cu(II) and 1.086, 1.044 and 1.741 for Ni(II) at the working temperatures, respectively. The increase in qmax values shows the accuracy of our study.

According to the measurements obtained, the adsorption kinetics of the adsorbent for both ion samples were found to be in accordance with the Ho-Mac Kay equation. The correlation coefficient of the results obtained for this equation was measured higher. This shows that the sensitivity is high for us.

ACKNOWLEDGEMENT

Dicle University Chemistry Department research laboratory was used for the experiments of this study. In addition, analyzes were made using the devices in the scientific research center of the university.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

REFERENCES

Baytar, O., Ceyhan, A. A., & Şahin, O. (2018). İğde Çekirdeğinden Elde Edilen Aktif Karbon Kullanılarak Sulu Çözeltilerden Pb(II) Adsorpsiyonun İncelenmesi: İzoterm ve Kinetik. *Bitlis Eren Üniversitesi Fen Bilimleri Dergisi*, *7*(2), 256-267. doi:10.17798/bitlisfen.422446

Bhattacharyya, K. G., & Gupta, S. S. (2008). Kaolinite and montmorillonite as adsorbents for Fe(III), Co(II) and Ni(II) in aqueous medium. *Applied Clay Science, 41*(1-2), 1-9. doi:10.1016/j.clay.2007.09.005

Borst, A. B., Smith, M. P., Finch, A. A., Estrade, G., Villanova-de-Benavent, C., Nason, P., Marquis, E., Horsburgh, N. J., Goodenough, K. M., Xu, C., Kynický, J., & Geraki, K. (2020). Adsorption of rare earth elements in regolith-hosted clay deposits. *Nature Communications*, *11*(1), 4386. doi:10.1038/s41467-020-17801-5

Dal, M. C., Onursal, N., Arıca, E., & Yavuz, Ö. (2021). Diyarbakır Karacadağ Kırmızı Tepe Skoryası ile Cu(II) Adsorpsiyon Kinetiğinin İncelenmesi. *Dicle Üniversitesi Mühendislik Fakültesi Mühendislik Dergisi*, *12*(2), 337-346. doi:10.24012/dumf.881650

Dawodu, F. A., & Akpomie, K. G. (2014). Simultaneous adsorption of Ni(II) and Mn(II) ions from aqueous solution unto a Nigerian kaolinite clay. *Journal of Materials Research and Technology*, *3*(2), 129-141. doi:10.1016/j.jmrt.2014.03.002

Eren, E. (2008). Removal of copper ions by modified Unye clay, Turkey. *Journal of Hazardous Materials*, *159*(2-3), 235-244. doi:10.1016/j.jhazmat.2008.02.035

Ewis, D., Ba-Abbad, M. M., Benamor, A., & El-Naas, M. H. (2022). Adsorption of organic water pollutants by clays and clay minerals composites: A comprehensive review. *Applied Clay Science*, *229*, 106686. doi:10.1016/j.clay.2022.106686

Fu, C., Zhu, X., Dong, X., Zhao, P., & Wang, Z. (2021). Study of adsorption property and mechanism of lead(II) and cadmium(II) onto sulfhydryl modified attapulgite. *Arabian Journal of Chemistry*, *14*(2), 102960. doi:10.1016/j.arabjc.2020.102960

Ho, Y. S., & Mckay, G. (1998). Kinetic Models for The Sorption of Dye from Aqueous Solution by Wood to Pollutant Removal on Various Sorbents. *Process Safety and Environmental Protection*, *76*(2), 183-191. doi:10.1205/095758298529326

Jiang, M., Jin, X., Lu, X.-Q., & Chen, Z. (2010). Adsorption of Pb(II), Cd(II), Ni(II) and Cu(II) onto natural kaolinite clay. *Desalination*, *252*(1-3), 33-39. doi:10.1016/j.desal.2009.11.005

Khan, U., & Rao, R. A. K. (2017). A high activity adsorbent of chemically modified *Cucurbita moschata* (a novel adsorbent) for the removal of Cu(II) and Ni(II) from aqueous solution: Synthesis, characterization and metal removal efficiency. *Process Safety and Environmental Protection*, *107*, 238-258. doi:10.1016/j.psep.2017.02.008

Mu'azu, N. D., Bukhari, A., & Munef, K. (2020). Effect of montmorillonite content in natural Saudi Arabian clay on its adsorptive performance for single aqueous uptake of Cu(II) and Ni(II). *Journal of King Saud University-Science*, *32*(1), 412-422. doi:10.1016/j.jksus.2018.06.003

Onursal, N., Dal, M. C., Kul, A. R., Yavuz, Ö. (2020). Cu(II) iyonlarının doğal karışık tipteki kil ile sulu ortamdan uzaklaştırılması, izoterm, kinetik ve termodinamik parametrelerin incelenmesi. *Eurasia Journal of Mathematics, Engineering, Natural & Medical Sciences*, *7(9)*, 85-103. doi:10.38065/euroasiaorg.84

Potgieter, J. H., Potgieter-Vermaak, S. S., & Kalibantonga, P. D. (2006). Heavy metals removal from solution by palygorskite clay. *Minerals Engineering*, *19*(5), 463-470. doi:10.1016/j.mineng.2005.07.004

Sarı, A., & Tüzen, M. (2009). Kinetic and equilibrium studies of biosorption of Pb(II) and Cd(II) from aqueous solution by macro fungus (Amanita rubescens) biomass. *Journal of Hazardous Materials*, *164*(2-3), 1004-1011. doi:10.1016/j.jhazmat.2008.09.002

Tirtom, V. N., Dincer, A., Becerik, S., Aydemir, T., & Celik, A. (2012). Comparative adsorption of Ni(II) and Cd(II) ions on epichlorohydrin crosslinked chitosan–clay composite beads in aqueous solution. *Chemical Engineering Journal*, *197*, 379-386. doi:10.1016/j.cej.2012.05.059

Yavuz, Ö., Altunkaynak, Y., & Güzel, F. (2002). Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite. *Water Research*, *37*(4), 948-952. doi:10.1016/S0043-1354(02)00409-8

Yavuz, O., Guzel, R., Aydin, F., Tegin, I., & Ziyadanogullari, R. (2007). Removal of Cadmium and Lead from Aqueous Solution by Calcite. *Polish Journal of Environmental Studies*, *16*(3), 467-471.