

Investigation of Adsorption of Landfill-Leachate Transport in Clay Soils

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Abstract

Leachates contained in most modern waste- containment facilities are aqueous solutions containing a complex mixture of inorganic and organic species. In the Turkey, solid wastes are primarily disposed in landfills. Landfills may potentially leak leading to contamination of underlying soils and groundwater. Compacted clays or mixtures of local soils with clay are frequently used to achieve very low hydraulic conductivity barriers and prevent subsurface contamination. In this study, experiments have been carried out to determine the adsorption capacity of the clay soils for some metal ions (Mn, Cu, Fe, Pb, Zn) in a batch reactor systems. For this purpose the leachate and clay soils was taken from Şile- Kömürçüoda Landfill Area on the Asian side of Istanbul. A series of experiments were carried out to determine the most efficient adsorbent amount with the leachate. In first step, the optimum amount of clay was determined by using clay in various amounts with constant amount of the leachate. In second step, the same amount of leachate was contacted with the optimum amount of clay in shaker to determine the effect of contact time. In last step, in order to determine the effect of temperature, all experiments were carried out at three different temperatures. In this study, after all experiments, the optimum amount of the clay was found 0.25 g. Depending on this result, optimum temperature was found 35 °C and recovery efficiencies up to 99 percent were achieved for Mn, Cu, Fe, Pb, Zn ions.

Keywords: Adsorption, clay soil, leachate, metal ions

Katı Atık Depolama Alanlarında Sızıntı Suyunun Killi Zeminden Geçerken Adsorpsiyonunun İncelenmesi

Öz

Sızıntı suyu çoğu katı atık depolama alanlarından kaynaklanan inorganik ve organik kompleks karışımını içeren sulu çözeltilerdir. Türkiye’de katı atıklar öncelikli olarak düzenli depolama sahalarında toplanmaktadır. Düzenli depolama alanları sızıntı yaparak yeraltı suyu ve toprağa potansiyel kirlilik kaynağı oluşturmaktadır. Sıkıştırılmış killer veya yerel topraklar ile kil karışımı sıklıkla çok düşük hidrolik iletkenlik bariyerleri elde etmek ve yüzey altı kirlenmeyi önlemek için kullanılır. Bu çalışmada, kesikli sistem ile bazı metal iyonları (Mn, Cu, Fe, Pb, Zn) ile kilin adsorpsiyon kapasitesini belirlemek için deneyler gerçekleştirilmiştir. Bu amaçla, sızıntı suyu ve kil İstanbul’un Asya yakasındaki Şile-Kömürçüoda Depolama Sahası’ndan alınmıştır. Sızıntı suyu ile en etkili adsorban miktarını belirlemek için bir dizi deney gerçekleştirilmiştir. İlk aşamada, sabit miktarda sızıntı suyu ile çeşitli miktarlarda kil kullanılarak optimum kil miktarı belirlenmiştir. Aynı miktarda sızıntı suyu, temas süresinin etkisini belirlemek için çalkalayıcıda optimum kil miktarı ile temas ettirilmiştir. Son adımda, sıcaklığın etkisini belirlemek için tüm deneyler üç farklı sıcaklıkta gerçekleştirilmiştir. Çalışmanın sonunda, tüm deneylerin ardından kilin optimum miktarı 0.25 gr bulunmuştur. Bu sonuca bağlı olarak Mn, Cu, Fe, Pb, Zn iyonları için optimum sıcaklık 35°C bulunmuş ve geri kazanım veriminde % 99’a kadar ulaşılmıştır.

Anahtar Kelimeler: Adsorpsiyon, kil, sızıntı suyu, metal iyonları

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1. Introduction

Heavy metals such as Fe, Cu, Mn, Zn, and Pb are present both in nature and in our bodies. These heavy metals, in nature and in our bodies, are slowly releasing to toxic effects. However, they can remain in the environment for centuries because of their conversion to other forms.

It causes diseases such as heavy metals, cancer, kidney diseases, liver diseases, growth retardation, joint diseases, nervous system diseases, Parkinson and Alzheimer's, autism, endocrine diseases, pregnancy anomalies and allergies which are accumulated especially in our body. Some of the factors that cause heavy metals to enter our bodies are industrial wastewater without treatment, pesticides, chemical drugs and heavy metals found in nature. These heavy metals accumulate by entering into our bodies, if they are used directly as drinking water or mixed with ground water and surface waters, directly or through the leachate in the landfills. Therefore, the treatment of such heavy metals is very important. One of the methods used for the treatment of heavy metals in storage areas that are exposed to leachate is adsorption.

Adsorption is used to remove individual components from a liquid mixture. The component to be removed is physically or chemically bonded to a solid surface [1]. Physical adsorption involves the attraction forces between the solid surface and the amount of adsorbed material.

For the substances to be removed, the adsorbent material must have a high adsorption capacity, a high mass transfer rate and a low deactivation rate. The high mass transfer rate is obtained by reducing the size of the adsorbed material particles [2]. According to the investigations, bark-tannin rich materials, lignin, chitin / chitosan, dead biomass, alginate, xanthate, zeolite, clay, fly ash, peat moss, bone gelatin beads, leaf mold, coated sand, modified wool, modified cotton etc. are determined as low-cost sorbents [3]. Clays are often used as pollution barrier for waste storage sites, given their high impermeability [4, 5 and 6] and, clays are abundant and cheap material successfully used for decades as an adsorbent for removing toxic heavy metals from aqueous solutions [7]. In most cases, the nature of clay that seals the site floor is a criterion for selecting the landfill site [6].

When considering the characteristics of the sorbents and the cost, clay supplied from İstanbul-Şile Komurcuoda was used as adsorbent material. Adsorption experiments were carried out via lab scale batch system. The aim of the work is to investigate the amounts of Fe(II), Mn(II), Zn(II), Cu(II), Pb(II) metal ions adsorbed by the adsorbent at different temperatures, different amount of adsorbent and different time conditions.

2. Materials and Methods

Clay soil and leachate were taken from Şile-Kömürçüoda Landfill Area on the Asian side of İstanbul. From wastewater pond in landfill area, obtained leachate sample. The leachate to result from landfill was stored at 4°C.

Adsorption Experiments

In this study, clay taken from the Şile-Kömürçüoda Area of İstanbul changing color from yellow to brown was used as an adsorbent [8, 9 and 10]. Adsorption experiments were carried out via lab scale batch system. The shaking process was carried out at a 100 rpm spin rate using a Zhicheng ZHWY-211B model shaking incubator.

In first step, the optimum amount of clay was determined by using clay in various amounts (0.1, 0.25, 0.5, 0.75 and 1 g) with constant amount of the leachate. 25 mL samples were shaken for 4 hours at 100 rpm. After 4 hours, samples were allowed to settle, samples were filtered using a 0.45 µm glass fiber filter and samples of the filtrate were collected and stored for analysis according to Standard Methods [11]. After all experiments, the optimum amount of the clay was found 0.25 g.

In second step, the same amount of leachate was contacted with the optimum amount of clay in shaker to determine the effect of contact time (2, 5, 10, 15, 30, 45, 60, 90, 120, 150, 180, 240 and 300 min.).

The results of chemical analysis of the clay and the characterization studies conducted on the leachate from the Şile-Kömürcüoda Area site are shown in Table 1.

Table 1. The chemical analysis of the clay used in Şile-Kömürcüoda Area [8-10].

Chemical Analysis (%)		Mineral Contents (%)		Sieve analysis (%)			
SiO ₂	51-54	Kaolinite	68-71	63 µm	100		
Al ₂ O ₃	27-29			40 µm	99		
Fe ₂ O ₃	2.5-2.7			Free	6-9	20 µm	98
TiO ₂	1.1-1.2					6 µm	91
CaO	0.1-0.2					2 µm	69
MgO	0.7-0.8	Illite	15-18	1 µm	47		
Na ₂ O	0.0-0.1						
K ₂ O	2.7-2.9	Others	2-5				
SO ₃	----						

In last step, in order to determine the effect of temperature, all experiments were carried out at three different temperatures (35, 45 and 60°C). Depending on this result, optimum temperature was found as 35 °C.

Fe, Mn, Cu, Pb and Zn ions were analyzed by PerkinElmer Atomic Absorption Spectrometer.

3. Result and Discussion

In first step, the optimum amount of clay was determined by using clay in various amounts (0.1, 0.25, 0.5, 0.75 and 1 g) with constant amount of the leachate. Leachate samples 25 mL samples were shaken for 4 hours at 100 rpm and 25°C. According to Fig. 1 the measured Fe(II), Mn(II), Zn(II), Cu(II) and Pb(II) concentrations of the leachate is 65.3, 1.33, 2.376, 1.499 and 0.536 mg/L. Removal rates of 95.32, 88.23 and 89.54 % were obtained for Fe(II), Mn(II), Zn(II) ions for leachate samples for 0.25 g adsorbent clay soil. Cu(II) and Pb(II) ions are not determined. Optimum adsorbent amount is 0.25 g was found for all metal ions.

Removal rates of 95.55 and 92.48 % were obtained for Fe(II) and Mn(II) of samples in 60 min. adsorption time. According to the Fig. 2, removal rates of 97.9 and 53.36 % were obtained for Zn(II) and Pb(II) of samples in 30 minutes adsorption time. Removal rate of 96.66 % was obtained for Cu(II) of sample in 45 minutes adsorption time. Removal rates decreased after these adsorption times. Removal rate behavior can be explained with adsorption criteria up to the 60 minutes and desorption afterwards. The optimum adsorption time for all metal ions in the leachate was selected for 60 minutes.

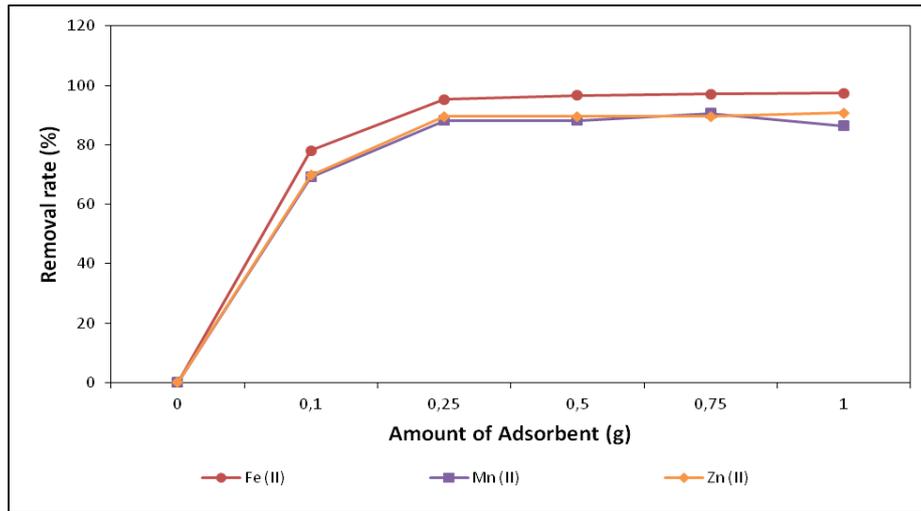


Figure 1. Effect of adsorbent amount on Fe(II), Mn(II) and Zn(II) ions adsorption by Şile-Kömürçüoda clay soil

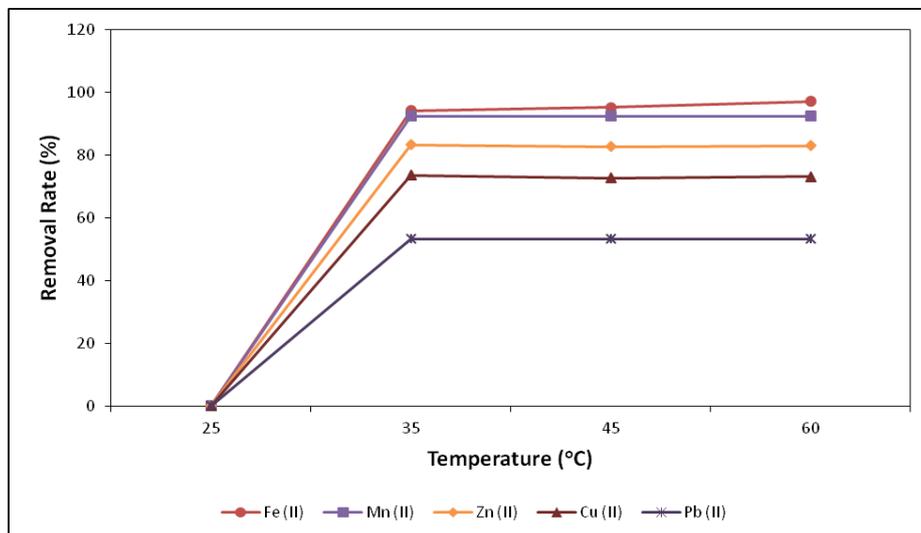


Figure 2. Effect of temperature on Fe(II), Mn(II), Zn(II), Cu(II) and Pb(II) ions adsorption by Şile-Kömürçüoda clay soil

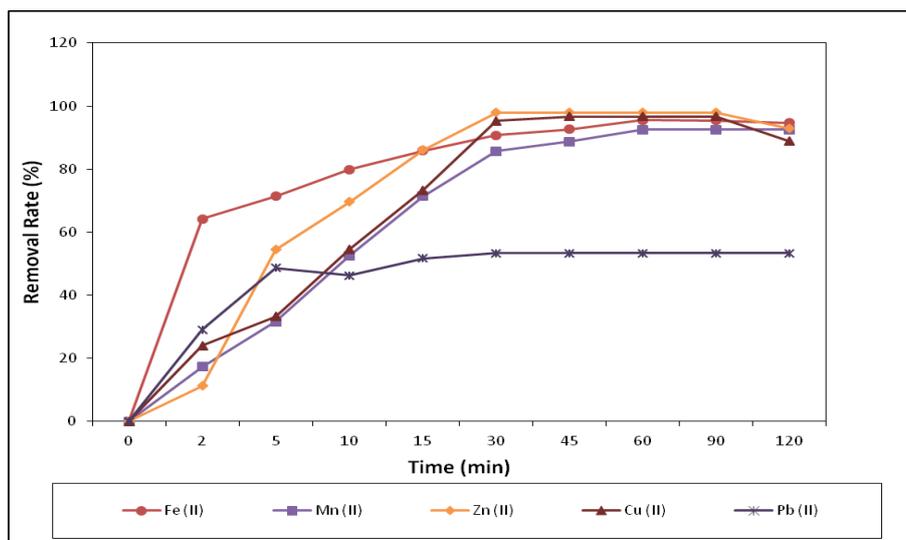


Figure 3. Effect of time on Fe(II), Mn(II), Zn(II), Cu(II) and Pb(II) ions adsorption by Şile-Kömürçüoda clay soil

In last step, in order to determine the effect of temperature, all experiments were carried out at three different temperatures (35, 45 and 60°C). Removal rates of 92, 83.38, 73.65 and 53.36% were obtained for Mn(II), Zn(II), Cu(II) Pb(II) ions for leachate samples in 35°C adsorption temperature (Fig. 3). Removal rate of 97.28 % was obtained for Fe(II) of sample in 60°C temperature. Depending on this result, optimum temperature was found as 35 °C for all metal ions.

Isotherms

To determine the different amount of metal ion concentrations on adsorption, isotherm experiments were carried out. During the period of study the pH level of the sample was adjusted to 6.5. The data derived from the adsorption isotherm experiments was applied to the Freundlich and Langmuir isotherm models, which are given as follows:

$$\log q_e = \log K_f + \frac{1}{n} \log c_e$$

where q_e is the adsorbed metal ion concentration (mg/g); C_e is the concentration of metal ion in the solution at equilibrium (mg/L); and K_f , the Freundlich affinity coefficient (mg/g). Based on the linear form of the adsorption isotherm obtained from plots of $\log C_e$ versus $\log q_e$, constants were calculated from the slope of the graph.

The other equation conforming to the results of the adsorption isotherm is given as:

$$\frac{c_e}{q_e} = \frac{1}{q_m K} + \frac{c_e}{q_m}$$

where q_e is the amount of adsorbed metal ion concentration (mg/g); C_e is the concentration of metal ion in the solution at equilibrium (mg/L); q_m is the capacity parameter (mg/g); and K , the Langmuir constant (L/mg).

Based on the linear form of the adsorption isotherm obtained from plots of C_e versus C_e/q_e , constants were calculated from the slope of the graph.

These Freundlich and Langmuir isotherm models have been widely used by researchers to account for the dosage effects when observing the adsorption of metal ions [12, 13]. Fig. 4 shows Langmuir and Freundlich type adsorption isotherms of clay taken from Şile-Kömürcüoda Area (metal ions at pH 6.5, 4 hours retention time, 25 mL leachate contacted with 0.25 g adsorbent).

For Fe ions R^2 , the correlation coefficient, of Langmuir is (0.9903) higher than the Freundlich isotherm (0.9203). That is the same case for the Mn, Zn and Cu ions. Their correlation coefficients of Langmuir are determined as (0.8486), (0.8244), (0.8933) that are higher than their Freundlich isotherm (0.8286), (0.5188), (0.6818). The case with Pb is the opposite of the described situation above. For Pb ions R^2 , of Freundlich is (0.9856) higher than the Langmuir isotherm (0.982).

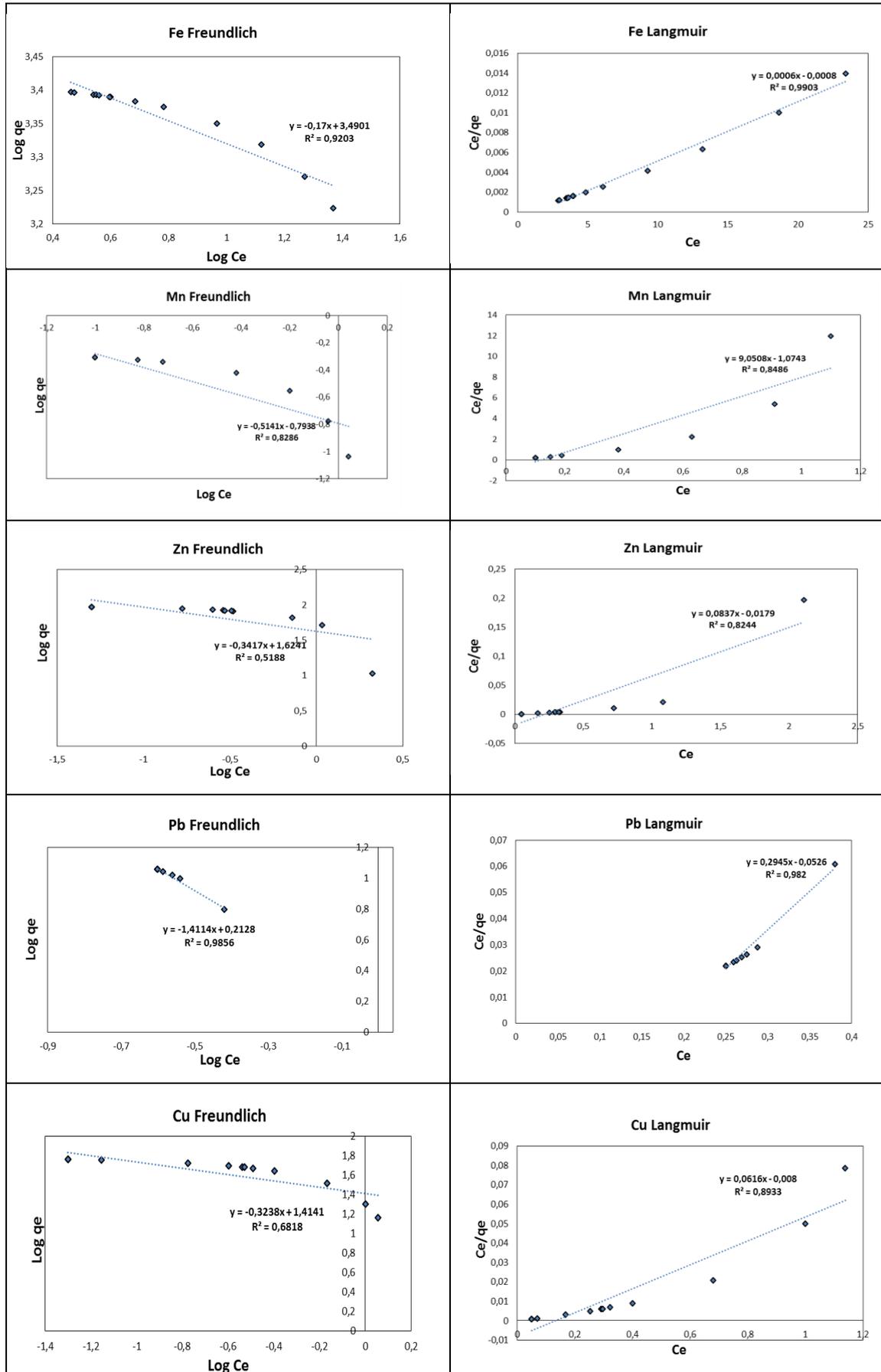


Figure 4. Langmuir and Freundlich isotherms of Şile-Kömürçüoda Area clay for Fe, Mn, Zn, Pb and Cu ions.

This study, carried out with metal ions based on the R^2 values shows that the Langmuir isotherm fits the experimental data better than the Freundlich isotherm.

4. Conclusions

Exceeding the limit values of metals found in natural environments such as soil, surface water and groundwater is undoubtedly a problem for nature and biological life. For this probing, in this study, it was ensured that the heavy metals in the leachate formed on the solid waste landfill would treatment an adsorbent. For this, parameters such as optimum temperature, amount of adsorbent and contact time are compared. In addition, the effect of the amount of adsorbent used in the adsorption of metal ions has been examined by Freundlich and Langmuir Isotherm Models.

According to the obtained results, the amount of adsorbent increased to a certain point, the removal of metals increased, but after a certain adsorbent amount, the removal efficiency remained constant. The temperature also increased to the extent of reaching 35 °C, but there was no change in the removal efficiency even though the temperature rose to 60 °C. When examined according to the adsorption times, it is determined that each metal was treated with an increased removal rate until a different contact time, but after a certain contact time the removal efficiency was constant.

In this study, it is shown that the Langmuir isotherm represents the experimental data better than the Freundlich isotherm.

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