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Investigation of Adsorption of Cu (II) Heavy Metal with Bentonite

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Abstract

In this study, adsorption of undesirable Cu (II) ion with bentonite in industrial wastewater was investigated at different temperature, pH and time intervals. Adsorption experiments were started with an adsorbent amount of 0.5 grams. Optimum pH determination experiments were carried out in the first stage of the adsorption experiments. The optimum pH determined after the experiments was determined as 5.0. Adsorption rates and adsorbed metal ions concentration increased with increasing concentrations of starting Cu (II) ions up to 25 mg / L and 500 mg / L in a medium containing 0.5 g of adsorbent. In the isotherm studies, isotherms were plotted and isotherm constants were calculated and it was clearly observed that the adsorption system, Langmuir and Freundlich isotherms. When the Gibbs free energy (ΔG) values calculated at different temperatures are taken into consideration, it is observed that the Cu (II) ions have negative values, for 100 mg/L and lower especially at low concentrations, and thus the reactions take place spontaneously for these concentrations. The compatibility of the adsorption system with the Langmuir and Freundlich isotherms was investigated, and it was observed that the adenomatoid system adhered to Langmuir and Freundlich. Based on the results, it is concluded that the amount of metal retained on the surface increases with temperature increase. Values (n> 1) were obtained for the experiments performed at each concentration of Cu (II) ions (up to 500 mg / L at 25 mg / L).

Keywords: Cu (II) ion, Bentonite, Adsorption**.**

Cu (II) Ağır Metalinin Bentonit ile Adsorpsiyonunun İncelenmesi

Öz

Bu çalışmada, endüstriyel atık sularda istenmeyen Cu (II) iyonunun bentonit ile adsorpsiyonu, farklı sıcaklık, pH ve zaman aralıklarında incelenmiştir. Adsorpsiyon deneylerine 0,5 gram adsorbent miktarı ile başlanmıştır. Adsorpsiyon deneylerinin ilk aşamasında optimum pH belirleme deneyleri yapılmıştır. Yapılan deneyler sonrasında belirlenen optimum pH 5,0 olarak belirlenmiştir. 0,5 gram adsorbent içeren ortamda, başlangıç Cu (II) iyonlarının derişimi 25 mg/L den 500 mg/L' ye kadar artmasıyla adsorpsiyon hızlarının ve adsorplanan metal iyonları derişimi arttığı görülmüştür. Ayrıca yapılan izoterm çalışmalarında ise izotermler çizilerek izoterm sabitleri hesaplanmıştır ve adsorpsiyon sisteminin, Langmuir ve Freundlich izotermine uyduğu açıkça gözlemlenmiştir. Farklı sıcaklıklarla yapılan deney sonuçlarında hesaplanan Gibbs serbest enerjisi (ΔG) değerlerine bakıldığında ise Cu (II) iyonlarının 100 mg/L ve daha düşük düşük derişimler deki tepkimelerinin negatif değere sahip olduğu ve bu nedenle belirtilen tepkimelerin kendiliğinden gerçekleştiğini gözlemlenmiştir. Adsorpsiyon sisteminin Langmuir ve Freundlich izotermlerine uyumluluğu araştırılmıştır ve sitemin hem Langmuir hem de Freundlich izotermlerine uyduğu gözlemlenmiştir. Bununla beraber sıcaklık artışı ile yüzeyde tutulan metal miktarının arttığı sonucuna varılmaktadır. Cu(II), iyonlarının her bir derişimde yapılan deneylerde (25 mg/L den 500 mg/L ye kadar) elde edilen bilgilerden (n>1) değerleri gözlenmiştir.

Anahtar kelimeler: Cu (II) iyonu, bentonit, adsorpsiyon.

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1. Introduction

The rapid increase in the production of various agricultural and industrial products in order to meet human needs is countering environmental problems that may lead to the degradation of ecological balance. We are faced with phenomena called air pollution, water pollution and soil pollution, which are generally polluted in areas where industrial facilities are concentrated. There are organic pollutants as well as inorganic pollutants in the wastes from environmental pollution. Heavy metals (such as Cu, Cd, Cr, Pb, Hg, Ni, Zn) from inorganic pollutants have a negative effect on living organisms even if they are found in the medium and they show toxic effect if they are present at a certain value [1,2].

In the case of environmental problems, the term "heavy metal" is often used as "a metal which has a relatively high density and is toxic or poisonous even at low concentrations", as if it were a very defined and precise group. This widespread belief is that accumulation of heavy metals in a living organism over a certain period of time relative to other metals leads to a gradual increase in the negative effect. In fact, the definition of heavy metals is used for metals with a physical density greater than 5 g / cm^3. This group includes more than 60 metals including lead, cadmium, chromium, iron, cobalt, Cu, nickel, mercury and zinc. These elements are usually present in the earth as a stabilizing compound in the form of carbonate, oxide, silicate and sulfur, or as imprisonment in silicates [3].

Cu (II) was used for the first time in the neolithic age and throughout history has been in many places in the daily lives of people. It has an atomic weight of 63,546 g/mol and an atomic number of 29, which has a high electrical and thermal conductivity, a reddish-brown, a soft and ductile structure and is easily formed. At present, it is known that Cu (II), which is industrially used for many purposes, is a heavy metal polluting water [4]. Cu (II), a metal naturally found in various rocks, in the soil, in water and in air, is also an element that plants, animals and people need to survive. It is known that adults require 2,0 mg Cu (II) per day. There are 0.8 mg Cu (II) in the human body [5]. Cu (II) plays an important role in the release of tissue iron in the formation of erythrocyte 7, bone, central nervous system and connective tissue development [6].

In this study, the availability of an alternative adsorbent for the removal of Cu (II) heavy metals in the wastewater has been investigated.

1.1. Adsorption

Adsorption can be defined as the increase of the material concentration by the bulk concentration at the interface (solid surface). Adsorption is divided into "physical adsorption" and "chemical adsorption" according to the types of force that keep the adsorbed on the surface. Interaction in physical adsorption occurs as a result of weak bonds and gravitational forces.. The force acting on the physical adsorption is the Van der Waals forces. Chemical adsorption is the result of a chemical reaction between the adsorbate and the absorbent, as a result of electron exchange. In physical adsorption, bonding forces are among molecules, while bonding forces in chemical adsorption are within molecules. The greatest advantage of physical adsorption against chemical adsorption is that it is reversible. That is, the physical adsorbent can be regenerated and reused, depending on the adsorbate that the chemical adsorbent interacts with the improvement. The rate of interaction in chemical adsorption depends on the temperature, while the interaction in physical adsorption is rapid [7]. The physical adsorption energy is therefore low and can be both single and multilayer, while the chemical adsorption energy can be high and monolayer.

1.2. Bentonite

Bentonite is versatile clay which is used industrial, agriculture, mining and engineering geology. The low cost and the abundant presence in our country, the increase in demand for this clay, makes bentonite interesting. Bentonite, which is composed of volcanic clay or glassy volcanic material such as tuff, with chemical decomposition and mainly montmorillonite group minerals, is a soft, shaped, light colored clay stone consisting of partially colloidal cysts [8].

1.3. Literature Review

Özcan (2010) studied the adsorption of Pb (II) by bentonite in a study. The study concludes that natural bentonite is an effective adsorbent for the removal of heavy metals from aqueous solutions [9].

Can et al., (2002) in a study of their study, The adsorption of bentonite on Lanasan Yellow CFB and Lanasan B rilliant Bine CF -BA paints was investigated. Experimantly, parameters are; calcination temperature, particle size, rotation per minute, adsorbant mass, initial dye concentration, pH and temperature. Thus by the results obtained from this parameters maximum adsorption of the dyes and theirs optimum conditions were investigated. Adsorption parameters for Langmuir and Freundlich isotherms were determined [10].

Ay et al., (2002) in a study of their study, adsorption of the Acid Yellow N2GIJ, Acid Red N2RBL, Basic Red 2L, Methylene Blue, Reactive Yellow RR, Reactive Red BB on bentonite were studied. Effects of various parameters such as, pH, agitation time, mixing rate, initial dye concentration, adsorbent mass and temperature on adsorption were investigated. The effects of these parameters on the maximum dye adsorption were determined. As a results, adsorption parameters for Langmuir and Freundlich isotherms were determined and discussed [11].

In this study, adsorption of Cu (II) with bentonite which is ready for use has been investigated. Then by using natural bentonite, adsorption process was run on Cu (II) ions which is a heavy metal causes water pollution. Adsorption is thermodynamically investigated by determining enthalpy exchange, entropy exchange, free enthalpy exchange and equilibrium constant during adsorption. In this view, an alternative solution to the removal of Cu (II) heavy metal, which is located in the wastewater and needs to be removed, has been investigated. Compatibility of adsorption system with Langmuir and Freundlich isotherms It was investigated. It has been observed that the system is compatible with Langmuir and Freundlich isotherms.

2. Material and Method

2.1. Preparation of Adsorbent

2.2.

The natural bentonite used in the experiments was obtained from Tokat region. Natural bentonite was first washed with deionized water, filtered through filter paper, It was taken into capsules and dried at 105 ^{o}C for 24 hours. The flask was then milled and sieved through a 55 µm sieve. At this stage, bentonite has taken its airborne nature into its own form. Finally the product was again dried at 105 ° C for 24 hours.

2.3. Concentration of Cu (II) ion

To determine the free Cu (II) ion concentration in the medium, Cu (II) was spectrophotometrically (DR 6000 model) assayed with the help of a brown colored complex of sodium diethyldithiocarbamate It is necessary that the Cu (II) ion can be complexed with sodium diethyldithiocarbamate and the pH of the medium must be above 9.0 to avoid the complex to break down. The solution was diluted to 10.0-100.0 mg / L Cu (II). 1 mL of the prepared sample, 20 mL of 1.5 N NH_3 and 0.2 mL of 1% sodium diethyldithiocarbamate were respectively stirred. This mixture was completed to a volume of 25 mL with distilled water. The absorbance was read at 460 nm in the spectrophotometer and the Cu (II) concentration in mg / L was switched from the working line [12,13]. The working indices used for the determination of the Cu (II) ion concentration are given in Figure 1 below.

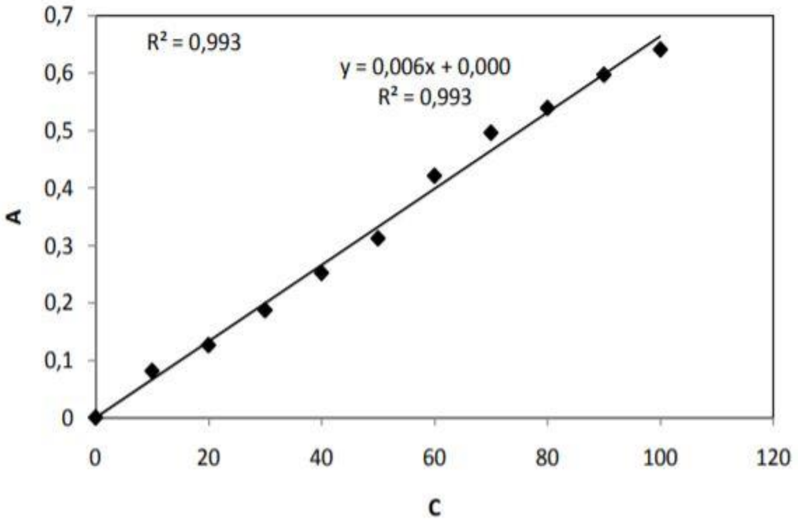

Figure 1. The working line used for Cu (II) ion concentration determination

2.4. Experiment of Adsorption Experiment

Adsorption experiments were carried out in reaction vessels operating in cut-off mode. As the reaction vessel, 250 mL erlenmeyer with a working volume of 100 mL were used. The 100 mL solutions prepared in the flasks were run at constant stirring speed and temperature with the mouths closed to prevent evaporation. Experimental work was carried out continuously in 250 ml sterilized erlenmeyer with a working volume of 100 mL at constant temperature and agitator running at a stirring speed of 150 rpm. Experiments were initiated by the addition of 0.5 grams of adsorbent in solution medium containing heavy metal. Experiments have been carried out at different temperatures after determining the optimum pH in metal ions and dyestuff experiments [14-16].

2.5. Analysis Methods

Adsorption experiments were initiated by adding a constant amount of 0,5 grams adsorbent. Then, after centrifuging the specimens taken from the test medium to the centrifuge tubes at specific time intervals, the liquid fraction was used to determine the concentration of the metal ions. In the adsorption experiments, the free Cu (II) concentration from the experimental medium containing Cu(II) was determined by spectrophotometrically reading the absorbance at 460 nm with the aid of a yellow-brown colored complex of Cu (II) ions with sodium diethyldithiocarbamate [12-14].

2.4.1. Mathematical Description of the Experimental System

2.4.1.1. Adsorption rate

The adsorption rate is defined as the slope of the tangent plotted at time t = 0 versus the time graph versus the amount of metal ions adsorbed by the mass of unit adsorbent.

$$r_{ad} = \frac{\Delta q}{\Delta t} \tag{1}$$

Where; rad: adsorption rate (mg adsorbed metal ion / g adsorbent/ min.)

q: the amount of metal ions adsorbed by the mass of unit adsorbent (mg metal ion / g adsorbent)
t : Time (minutes)

$$q = \frac{C_o - C}{X} \tag{2}$$

Where; Co: Initial metal ion concentration (mg metal ion / L solution)
C: Concentration of metal ion remaining after adsorption in any adsorption medium (mg metal ion / L solution)
X: Concentration of adsorbent in solution (g adsorbent / L solution)

2.3.1.2. Adsorption yield

Adsorption yield is defined as the ratio of the concentration of the metal ion adsorbed by 1 g of adsorbent per liter to the initial metal ion concentration in the equilibrium, in the case of a single metal ion.

$$\%Ad = \frac{C_{Ad,d} / X}{C_o} \tag{3}$$

Where; $C_{Ad,d}$: Concentration of metal ion adsorbed by the equilibrium microorganism (mg metal ion / L solution).

2.4.1.3. Mathematical description of adsorption equilibrium

Adsorption is an equilibrium process and lasts until dynamic equilibrium is reached between the adsorbed concentration remaining in the solution and the adsorbed concentration held on the solid surface. In this case, the adsorbent has a certain distribution between solid and liquid phases. In order to indicate the adsorption equilibrium, the amount of adsorbed amount of adsorbent per unit weight is plotted against the adsorbent concentration remaining in the equilibrium solution at constant temperature. Generally these non-linear curves are called "adsorption isotherms".

The main models which express mathematically the adsorption equilibrium in single component systems are Langmuir and Freundlich models.

Langmuir model

According to the Langmuir model, there is a fixed number of active adsorption centers on the adsorbent surface, all of which are at the same energy level and the adsorbed components form a single saturated layer on the adsorbent surface. Moreover, according to this model, the adsorption balance is a dynamic equilibrium and the molecules attached to the surface do not interact with each other. The Langmuir model is given in Equation 4.

$$Q_{den} = \frac{Q_o b C_{den}}{1 + b C_{den}} \tag{4}$$

Where; q_{den}: Amount of the substance adsorbed by the unit adsorbent mass (mg / g)

C_{den}: Concentration of adsorbed material remaining in solution before adsorption (mg / L)

b: A constant (L / mg) indicating the adsorbent interest and the strength of bond between the adsorbate and adsorbent associated with adsorption enthalpy.
Q_o: The amount of component adsorbed per unit mass of adsorbent (mg / g) to form a complete monolayer on the surface.

Linearization of the Langmuir model given in Equation 4 yields Equation 5 given below.

$$\frac{C_{den}}{q_{den}} = \frac{C_{den}}{Q_o} + \frac{1}{bQ_o} \tag{5}$$

The gradient 1 / Q^o of the C_{den} versus C_{den} / Q_{den} gives the y- axis cutting point 1 / bQ^o. The size of Q_o and b indicates high adsorption capacity. If adsorption is very low, ie b $C_{den} << 1$, the amount of adsorbed material per equilibrium unit adsorbent is proportional to the amount of adsorbed material in the solution.

$$q_{den} = Q^o b C_{den} \tag{6}$$

In the case of excess adsorption, $bc_{den} >> 1$, the amount of adsorbed material per equilibrium unit adsorbent remains constant and is expressed by Equation 7.

$$q_{den} = Q^o \tag{7}$$

Freundlich model

The Freundlich model is described for heterogeneous surface energies that vary depending on the adsorption heat. This model expresses a special case where the energy term (b) in the Langmuir adsorption equation changes as a function of the surface coverage (q) and is defined by Equation .8:

$$q_{den} = K_F . C_{den}{}^{1/n} \tag{8}$$

Where; K_F: The adsorption constant (L $^{1/n}$ mg $^{1-1/n/g}$), which indicates the size of the adsorption capacity, depending on the adsorbent and adsorbed component,

n: The adsorption degree showing the degree of adsorption.

The linearized form of Equation 8 is given by Equation 9:

$$\ln q_{den} = \ln K_F + \frac{1}{n} \ln C_{den} \tag{9}$$

1n is the slope of the $\ln C_{den}$ versus ln Q_{den}, and $\ln K_F$ is the cutoff point of the y-axis. The Freundlich equation has n> 1 and the n and K_F parameters usually decrease with increasing temperature. The large values of K_F and n indicate that the adsorbent is prone to adsorption and has a high adsorption capacity.

As the Langmuir and Freundlich adsorption models characterize the adsorption from mathematically diluted solutions, adsorption data at mean concentration intervals are compatible with both isotopes. The Freundlich model is a more realistic approach than the Langmuir model because it contains different active binding centers on heterogeneous surfaces [15-22].

Comparison of Langmuir isotherm and Freundlich isotherm: The Langmuir isotherm is a theoretically derived equation, the Freundlich isotherm is an experimentally derived equation. While assuming adsorption and desorption of adsorbate molecules in the Langmuir isotherm to be reversible, no assumption is made in the Freundlich isotherm. The Langmuir isotherm is typically well matched to the experimental data of the individual components, while the Freundlich isotherm is well compatible with the experimental data obtained from the mixture of the components [23].

3. Results

3.1. Initial pH Effect

The pH of the adsorption medium is one of the important parameters in the adsorption of heavy metal ions. In Fig. 2, Cu (II) ions have adsorption results with bentonite. An increase in adsorption up to pH 5.0 was observed at the obtained pH range. In the experiments made after pH 5.0, precipitation was observed, e.g, bentonite did not adsorb at pH values higher than 5. For this reason, adsorption experiments with bentonite were continued at pH 5.0.

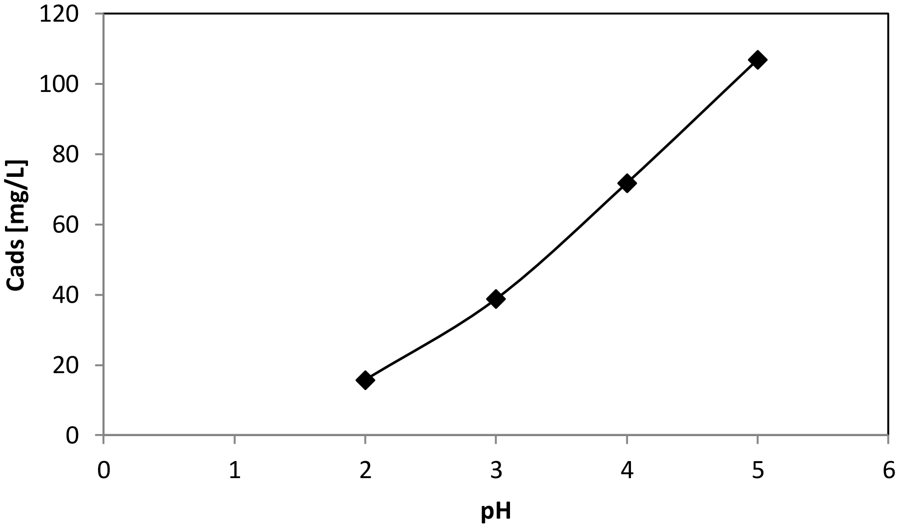

Figure 2. Adsorption-induced effect of initial pH on the adsorption of Cu (II) ions for Bentonite (T: 23 ° C)

3.1.1. Effect of initial Cu (II) ion concentration on adsorption rate, amount of adsorbed matter and change of Cu (II) ion concentration over time

When the effect of Cu (II) ion concentration on the adsorption rate of pH 5.0 initial Cu (II) ion concentration is investigated in Fig. 2, it is seen that the adsorption rate increases and the yield is at pH 5.0 .

When the initial Cu (II) ion concentration on the amount of adsorbed material is investigated in the experiment with bentonite at pH 5.0 in Fig. 3, it is observed that the amount of adsorbed material increases as the initial Cu (II) concentration increases. A reduction in the amount of adsorbed material was observed after about 350 ppm, but the adsorption was continued as the amount of concentration, the driving force, was increased.

In Fig. 4, concentration-time plots are given to investigate the effect of Cu (II) adsorption on the contact time. After about 1 hour from the adsorption system of the graphs, there is no increase in the adsorbed Cu (II) concentration, that is, the adsorption process is in balance. In Fig. 4, it was determined that the adsorbent adsorbed Cu (II) ions (25-100 mg / L) in low concentrations in less than 1 hour and the system reached equilibrium.

In Fig. 4, it was determined that adsorption of Cu (II) ions by bentonite in low concentrations (25-100 mg/L), shorter than 1 hour while concentrations of 250 and 500 mg/L last 1.5 hours.

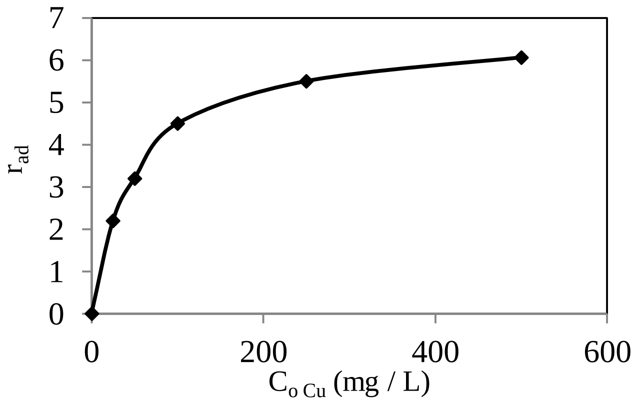

Figure 3. Effect of initial Cu (II) ion concentration on adsorption rate at pH 5.0 for bentonite

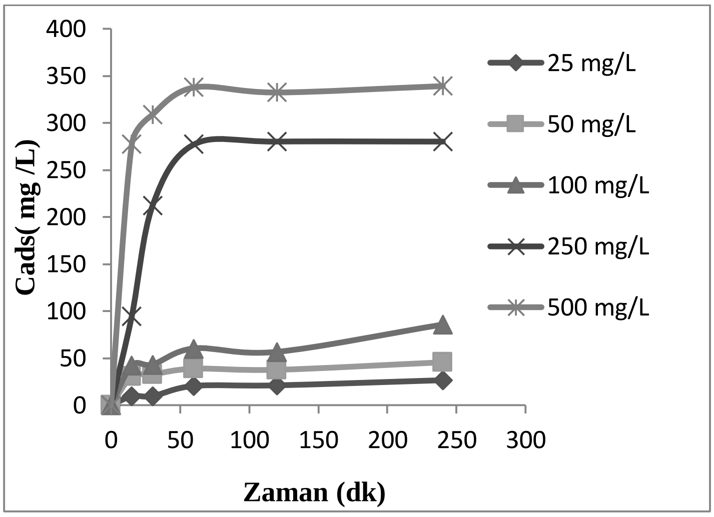

Figure 4. Adsorption-time graph of Cu (II) ions with bentonite

3.1.2. Obtaining adsorption isotherms for Cu (II) ion and calculation of adsorption constants

The adsorption isotherms of Langmuir and Freundlich isotherm equations obtained at pH 5.0 and 23 °C are presented in Fig. 5 and Fig. 6, respectively. Langmuir and Freundlich adsorption constants at the same pH and temperature are presented in Table 1.

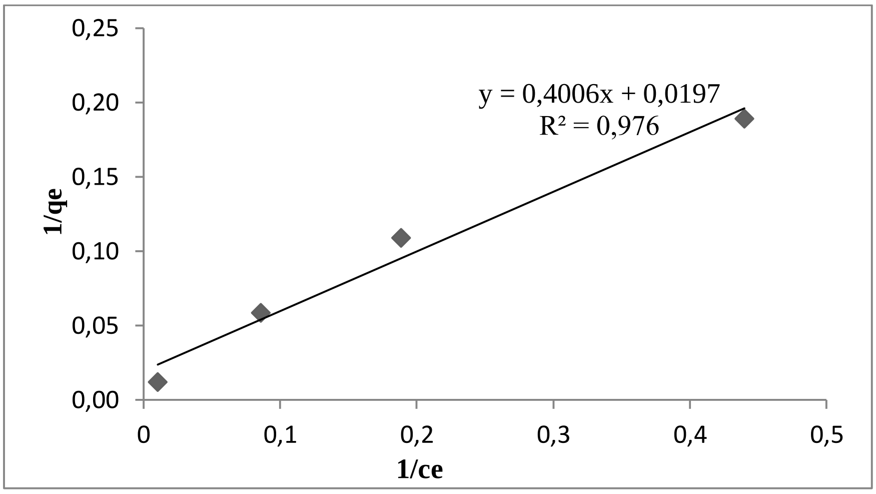

Figure 5. Adsorption isotherm obtained by linearization of the Langmuir adsorption isotherm equation at pH 5.0 for bentonite and Cu (II) (T: 23 ° C)

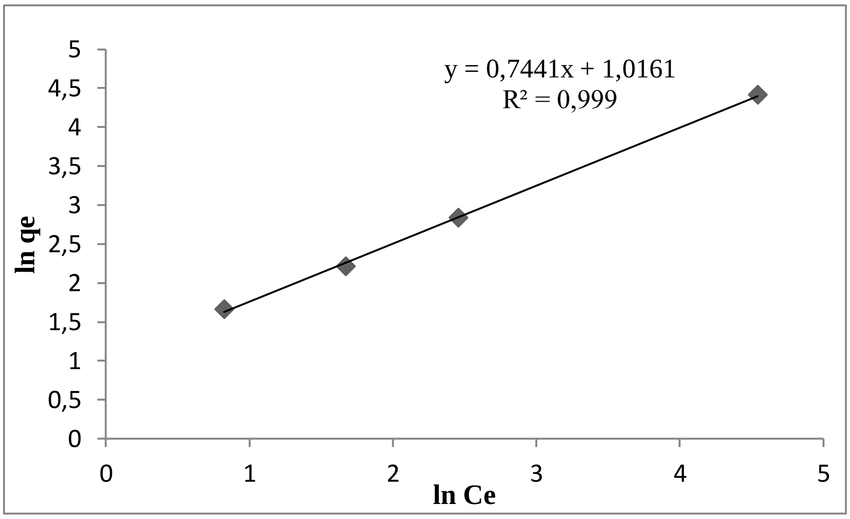

Figure 6. Adsorption isotherm obtained by linearization of Freundlich adsorption isotherm equation at pH 5.0 for bentonite and Cu (II) (T: 23 ° C).

Table 1 shows the Cu (II) adsorption, the constants obtained from the Langmuir and Freundlich isotherms are obtained for bentonite at different temperatures. Table 1 shows the Langmuir and Freundlich isotherm constants of Cu (II) adsorption by bentonite at different temperatures. If n is between 1 and 10, then it is thought to be a good adsorption. The 1 / n value of the 1 / n expression at the Freunlich isotherm is the heterogeneity factor. Here Freundlich isotherm constants show that the values of n, which is a constant, are higher than 1, and that implies that the adsorption takes place under appropriate conditions.

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Table 1. Langmuir and Freundlich adsorption constants obtained from Langmuir and Freundlich adsorption isotherms obtained at different temperatures for the adsorption of Cu (II) ions with bentonite

Temperature	**Langmuir**		**Freundlich**	
(^{0}C)	**Q^0 (mg/g)**	**b (L/mg)**	**K_F (L/g)**	**n**
23	52,63	0,047	2,762	1,3440
30	35,71	0,080	4,540	2,1645
35	45,45	0,040	3,607	1,7857
40	45,45	0,054	4,284	1,9723

Table 2. Thermodynamic data for the adsorption of Cu (II) ions with bentonite

Cu (II) concentration	**T (^{0}K)**	**ΔG (kJ /mol)**	**ΔH (kJ /mol)**	**ΔS (J/mol x K)**	**R^2**
25 mg/L	296	-2074,76	-61050	-200,7	0.999
	303	-2270,16			
	308	-1266,03			
	313	-2010,49			
50 mg/L	296	-1342,83	-26097,6	92,7	0.968
	303	-2792,10			
	308	-2652,01			
	313	-2851,24			
100 mg/L	296	-939,52	-64882,5	-201,1	0,933
	303	-4176,70			
	308	-2364,49			
	313	-2181,94			
250 mg/L	296	7488,69	9793,8	-941,9	0.999
	303	2184,51			
	308	1565,79			
	313	1929,792			
500 mg/L	296	331,239	23936,0	58,1	0.942
	303	6393,591			
	308	5814,62			
	313	5817,85			

Positive values of enthalpy (ΔH) indicate that the adsorption is endothermic while the negative values of Gibbs free energy (ΔG) indicate that the adsorption is spontaneous. Positive values of entropy (ΔS) indicate the increase in randomness at the solid/solution interface.

Table 2 shows the thermodynamic data obtained by adsorption of Cu (II) ions with bentonite. Gibbs free energies (ΔG) calculated at some concentrations with the help of the obtained data appear to be negative for cases where Cu (II) solution lower than 250 mg/L. These values show us that the adsorption phenomenon takes place spontaneously. The enthalpy values calculated for the adsorption system indicate that the system is endothermic or exothermic. Here, the enthalpy results of the adsorption system at low Cu (II) concentrations are positive in experiments with bentonite. This shows us that the system is endothermic for low concentration conditions. The negative enthalpy results indicate that the system is exothermic [21]. In this study, reactions up to 250 mg / L were carried out endothermically. Entropy (ΔS) is a measure of irregularity. Table 2 also showed positive results for concentrations of 50 and 500 mg / L.

According to the results obtained from Cu (II) adsorption experiments with bentonite, Gibbs free energy is given to be negative till 250 mg/L concentrations and again shows that the adsorption system is spontaneous. In the echolalia results, the system is endothermic and when the results are negative then, the system is exothermic. In the same way, Canbaz (2014) showed that ΔG values were found to be negative at all concentrations (25-500 ppm) in Cu adsorption experiments with activated sludge [24]. However, Cu adsorption studies of Tekin (2013) with sepiolite showed negative values in the range of 25-250 ppm and positive values in the range of 500-1000 ppm [56]. Similarly, in the study of Tok (2009) the calculated ΔG values for adsorption of Cu with zeolite were found to be negative in all different temperature studies (298-318 K) [26]. In this study, the performance of the reactions is determined, depending on the varying concentrations and temperatures during the experiments. As a result, it is seen that adsorption process between bentonite and Cu (II) occurs spontaneously for concentrations lower than 250 mg/L. When experimental results are compared with previous studies, it has been found that the thermodynamic data at different temperature and concentration ranges have different values and different results.

4. Conclusion

Adsorption experiments were started at ambient temperature of 23 ° C and the effect of temperature on adsorption was investigated by increasing the temperature at certain intervals. The adsorption process in a slurry batch reactor is a single step equilibrium separation process, and equilibrium curve and operating line equations must be known in order to proceed mass balancing and reaction vessel design of this process. Based on the criteria, in this study, equilibrium equations and other thermodynamic parameters in one component system are calculated. The adsorbent was bentonite and Cu (II) solution was used as adsorbate. Isotherm constants were calculated by drawing isotherms for the Cu (II) ion and it was found that the adsorption system showed compatibility with both Langmuir and Freundlich isotherms. Consequently, depending on the thermodynamic parameters it is seen that adsorption process between bentonite and Cu (II) occurs spontaneously for concentrations lower than 250 mg/L.

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