

Removal of Cobalt Ions from Aqueous Solution by Diatomite

Ali Rıza Kul, İhsan Alacabey, Necla Çalışkan Kılıç*

Yüzüncü Yıl University, Faculty of Science and Letters, Department of Chemistry, Van, Turkey

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Abstract

Diatomite ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) is a soft, light-color slightly sedimentary rock formed from accumulation of siliceous crusts of diatoms, which are aquatic organism from algae, and have fossil characteristics. In this study, the diatomite obtained from Çaldıran/Van-Turkey was tested as adsorbent for Co(II) ions adsorption from aqueous solution. Mineralogical and chemical characteristics of the diatomite, which its surface characteristics had been changed by modifying it with MnO_2 (Mn-diatomite), were evaluated. Effects of surface modification, pH of the solution, temperature, initial concentration of Co(II) ions were investigated on the adsorption of Co(II) ions on natural and modified diatomite as a function of temperature. Experimental data were applied on Langmuir and Freundlich adsorption isotherms and model parameters were determined. Adsorption enthalpy (ΔH), Gibbs free enthalpy (ΔG) and adsorption entropy (ΔS) values were calculated from thermodynamic analyses.

INTRODUCTION

Diatomite ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) is a soft, light-color slightly sedimentary rock formed from accumulation of siliceous crusts of diatoms, which are aquatic organism from algae, and have fossil characteristics [1]. It is used in many industrial areas as filtering-utility material, filling material, insulation material, adsorbent, abrasive material and surface cleaning material, catalyst carrier, light construction material and silica source in chemical material manufacturing because of its physical and chemical characteristics [1,2]. Its usage for filtering is highly prevalent

because of its porous structure, low density, high surface area, chemical inertness and being sterile [3]. It is used in filtration of raw sugar syrup, beer, whiskey, wine, water of swimming pool, pharmaceuticals, industrial wastes, chemical materials, mineral and vegetable oils as well as for microbial pollution such as bacteria, virus, protozoa from drinking water and plasma from human blood [4].

Active centers of diatomite having active hydroxyl groups on its surface responsible for adsorption may be characterized as the following: (i) insulated free silanol groups ($-\text{SiOH}$), (ii) free dual silanol groups ($-\text{Si}(\text{OH})_2$), (iii) $-\text{Si-O-Si}$ bridges with oxygen atoms on the surface. Silanol groups are active and have a tendency to react with many polar organic compounds and various functional groups [5]. Therefore, they are used as adsorbent in heavy

* Correspondence to: Necla Çalışkan Kılıç

Yüzüncü Yıl University, Faculty of Science and Letters,
Department of Chemistry, Van, Turkey

Tel: +90432 225 1256; Fax: +90432 225 1256

E-mail: ncaliskan7@hotmail.com

metal and dye removal studies. Adsorption capacity and filtration rate of diatomite have been improved by thermal process and various chemical applications. One of these processes is to change surface characteristics of diatomite by modifying it with MnO₂ (Mn-diatomite). Adsorption capacity of Mn-diatomite for metal cations is higher than that of natural diatomite depending on its high negative surface charge [6].

Inorganic contamination, especially heavy metal ions are responsible for water pollution mainly. Most of them have toxic and carcinogenic characteristics and they threaten human health and aquatic environment seriously when they enter into water. Heavy metals are used in processing raw materials in many branches of industry. Cobalt enters into the environment through natural resources and burning of coal, petrol or cobalt-alloys. It is been as particles in the air and bound by falling onto water or soil within a few days. Some cobalt compounds can dissolve in water. It does not disappear in the environment but changes its form. The only reason for increase in amount of radioactive cobalt in the environment is radioactive decomposition. A small amount of cobalt is had by respiration, food and drinking water. It may be both useful and also harmful for human health [7-17]. It is accumulated in liver mostly. In case of high-level intakes, it may cause lung, heart, liver, kidney and skin diseases in humans and animals. It has been reported that non-radioactive cobalt intake even in high levels by food and drinking water does not cause cancer in humans and animals. However, it was seen that it causes cancer when it was supplied by respiration or applied by vascular injection or introduced under muscles or skin in the experiments on animals and accordingly, it was reported that it may be carcinogenic for humans. High-level cobalt radiation may cause some cancer types develop by changing genetic materials in cells [8,9]. Adsorption is one of the methods used in removing heavy metals from

aqueous solutions. Therefore, diatomite having a local raw material resource was employed and the study was evaluated according to the followings. Firstly, Co(II) ions adsorption from aqueous solution onto natural and MnO₂-modified diatomite and the effect of surface modification on adsorption capacity were investigated. Then, the effects of pH, temperature and initial concentration on the adsorption capacity were determined. after that, Langmuir and Freundlich adsorption models were applied to adsorption data. Finally, thermodynamic parameters were calculated.

MATERIAL AND METHOD

In the present study, diatomite from Çaldıran/Van-Turkey, which its chemical composition was analysed by XRF and given in Table 1, was employed. The sample is composed of plaque and circular-shape diatomite particles with sizes of 0.005-0.025 mm in clay matrix according to the thin cross-sectional analysis applied on the diatomite rock taken from the region. Natural diatomite sample, which was powdered by pounding in a porcelain mortar, was washed by distilled water and dried in a drying oven at 105°C and then, put into polyethylene bags and stored to use in the future.

Table 1. Chemical composition (%) of the diatomite from Çaldıran/ Van-Turkey.

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	Na ₂ O	K ₂ O	LoI ^a
69.70	11.50	4.40	0.65	0.80	1.40	11.55

^aLoss of ignition at 1025°C.

Surface Modification

15 g of diatomite sample was mixed with 6 M NaOH at 80°C for 2 hours. MnCl₂ was added into the mixture. The pH of the mixture was adjusted to around 1-2 by using HCl. then, the mixture was stirred for 10 hours at room temperature. In order to increase the manganese hydroxide formation rate,

the diatomite was re-mixed with 6 M NaOH at room temperature for 10 h and then, decanted and left subject to air for oxidation. The sample was washed by distilled water and dried in a drying oven at 105°C and then, it was powdered by pounding in a porcelain mortar. It was put into polyethylene bags with "Mn-diatomite" label and stored to use in the future [6]. The effect of surface modification was characterized by infrared spectrophotometer (FT-IR Spectrophotometer, Bio-Rad Win-IR).

Adsorption

Natural and Mn-diatomite samples were grinded in separate mills. Then, particle size was lowered by the help of 230-mesh sieve. In adsorption equilibrium studies, 0.1 g natural and modified diatomite samples were treated with 5 mL cobalt solution. The mixtures in 5, 15 and 25 mg/L

concentrations and containing $\text{Co}(\text{NO}_3)_2$ solutions were shaken by temperature-controlled automatic shakers at 298, 303 and 313 K and by keeping pH at 2.5, 4 and 7 in various time periods. pH of the solutions were adjusted with the help of 1 M HCl or 1 M NaOH. The measurements were performed by Henna pH 211 pH-meters. All chemicals employed in surface modification of MnO_2 and diatomite and adsorption experiments were pure analytically and supplied by Merck. All adsorption measurements were performed by Solaar AA M Series v1.23 model spectrometer.

RESULTS AND DISCUSSION

Characterization of the Adsorbent

According to the FT-IR data of original and Mn-diatomite (Figure 1), spectral band density of diatomite was observed at 3624 cm^{-1} , 1094 cm^{-1} and 797 cm^{-1} . The band at 3624 cm^{-1} is related to free silanol groups (Si-OH) on the surface. The bands of 1094 cm^{-1} and 797 cm^{-1} belong to Si-OH stretching vibrations and Si-OH flexion, respectively. It is seen that the densities disappeared in the bands of 3624 cm^{-1} ve 1094 cm^{-1} after modification as a result of chemical interaction between silanol group on the surface and oxides. The bands of 1457 cm^{-1} and 1010 cm^{-1} are Si-O tension bands. Disappearing of OH bands after modification indicates that modification is done well.

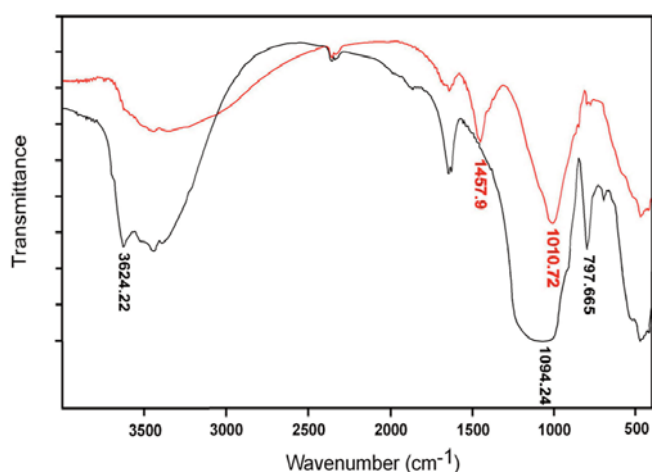


Figure 1. FT-IR spectra of natural and modified diatomite (black line: natural diatomite, red line: modified diatomite).

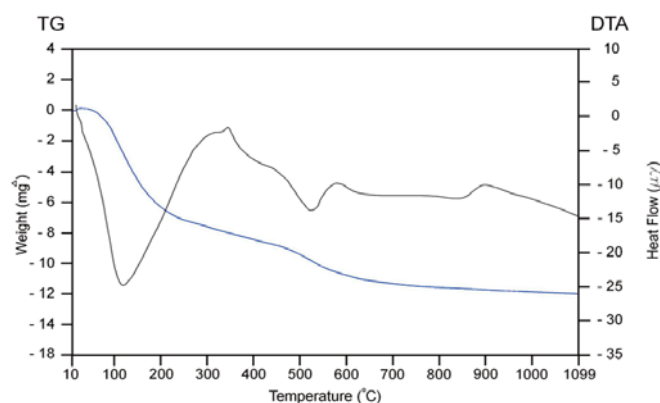


Figure 2. DTA-TG curve of original diatomite.

The endothermic peak between 100 and 400°C belongs to dehydration and the endothermic peak between 500 and 600°C belongs to de hydro-oxy-silation and the exothermic peak between 900 and 1000°C belongs to falling down of crystal roof according to the DTA curves of original diatomite found in clay matrix and shown in Figure 2.

Table 2. Langmuir and Freundlich parameters determined for adsorption of Co(II) ions on original diatomite.

pH	T (K)	Langmuir			Freundlich		
		K (L/mol)	q _m (mol/g)	R ²	n	k _f (mol/g)	R ²
2.5	298	-160.03	32.80	0.9992	0.9337	79.71	0.9960
4	298	935.13	636.11	0.9994	1.9106	0.47	0.9504
7	298	-3920.56	438.19	0.9899	0.4223	8.50 E+11	0.9428
2.5	303	661.06	62.28	0.9969	1.2464	4.39	0.9970
4	303	704.57	575.53	0.9839	1.9503	0.42	0.8809
7	303	1521.86	69215.97	0.9745	3.5546	0.04	0.8717
2.5	313	-292.45	32.05	0.9989	0.9348	79.94	0.9983
4	313	951.30	679.28	0.9989	2.0185	0.33	0.9352
7	313	-5367.15	430.08	1.0000	0.3492	2.31 E+15	0.9846

Adsorption Isotherms

The adsorption of cobalt ion on natural and modified (Mn-diatomite) diatomite at 298, 303 and 313 K were studied at pH 2.5, 4 and 7. When the adsorption of cobalt ions on natural and modified diatomite was evaluated as a function of time, it was found that time required for that adsorbed heavy metal amount achieved to a constant was equilibrium time and the adsorption achieved to equilibrium in approximately 90 minutes in the experiments performed. The parameters affecting cobalt ion on natural modified diatomite from aqueous solution were examined and optimum intake conditions were determined. It was observed that adsorption capacity varied by pH value of the solution, concentration of Co(II) ions solution, mixing time and temperature.

Equilibrium studies are required for determining constants of adsorption isotherms, which are important in determining adsorption capacity and especially describing surface characteristics of adsorbent [10]. Experimental data were evaluated by Langmuir and Freundlich adsorption models given by (1) and (2) equations, respectively.

$$1/q_e = 1/q_m + 1/(q_m \cdot K \cdot C_e) \quad (1)$$

$$\ln q_e = \ln k_f + n \cdot \ln C_e \quad (2)$$

C_e is the equilibrium concentration of the solution

(mol/L); q_e is the amount of arrested material on the adsorbent's surface in equilibrium (mol/g); q_m is the maximum amount of arrested material on the adsorbent's surface in equilibrium (mol/g), K is Langmuir constant; equilibrium constant of adsorption (L/mol), n is Freundlich constant, k_f is Freundlich constant (mol/g). Tables 2 and 3 show Langmuir and Freundlich parameters determined for original and Mn diatomite respectively.

According to the data shown on Tables 2 and 3, the correlation factor values (R²) of Langmuir model are higher than that of Freundlich model. Thus, Co(II) adsorption on original diatomite correlates better with Langmuir isotherm. The same is true for modified diatomite also in general manner. That R² values yield a value like 0.99 supports that adsorption centers exists in a limited number on the diatomite surface and the theory that Co(II) ion is adsorbed with maximum capacity as monomolecular on the surface.

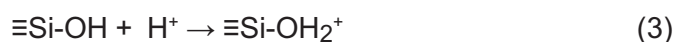
It is seen in Tables 2 and 3 again that some of Langmuir parameters have negative values. The reason may be the character of the adsorption event occurred in the media. The adsorption event seen here might occurred by the electrostatic attraction force between various dissolved ions found in the media and the adsorbent's surface. Although these negative values are not a usual situation, it is possible to encounter such kind of results [11,12].

Table 3. Langmuir and Freundlich parameters determined for adsorption of Co(II) ions on Mn-diatomite.

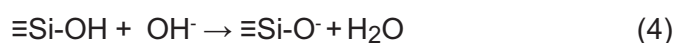
pH	T (K)	Langmuir			Freundlich		
		K (L/mol)	q _m (mol/g)	R ²	n	kf (mol/g)	R ²
2.5	298	-519.41	34.75	0.9978	0.8793	209.24	0.9976
4	298	6189.92	-6529.88	0.9533	-0.8651	1.75 E-12	0.7110
7	298	-4152.18	1763.37	0.9993	0.4051	1.29 E+14	0.9798
2.5	303	447.80	163.48	0.9998	1.2039	14.88	0.9996
4	303	1205.23	51384.38	0.9971	2.4604	0.48	0.9649
7	303	12673.79	-420.52	0.8618	-0.3622	2.54 E-22	0.7717
2.5	313	590.81	208.22	0.9992	1.2801	8.91	1.0000
4	313	5231.48	-7282.82	0.6219	-1.1985	5.19 E-10	0.9319
7	313	8.02	5519.95	0.9800	0.9725	8910.68	0.9205

The Effect of pH on Adsorption

Surface charges of diatomite may form by chemical reactions on the surface depending on ionisable functional groups such as -OH, -COOH, -SH [13]. In case of oxides and hydroxides, the surface is charged by [SiOH₂⁺] and [SiO⁻] ionizations. This is called as surface charge density. Surface charge density depends on pH of the media. The charges from cations and anions are equal and total charge is zero at zero charge point. Hydroxyl groups on the surface of the diatomite may gain or lost proton by changing of pH [13]. The surface gains proton and is charged positively at low pH values.



Hydroxides on the surface lost proton and the surface is charged negatively at high pH values.



Considering that active center for adsorption is SiO₂, diatomite surface charge is given as zero at pH 4 and Mn-diatomite's surface charge is given as -40 μcoule/cm² [6,14]. Surface charge of MnO₂ is higher than those of other oxides such as SiO₂, TiO₂, Al₂O₃ and FeOOH depending on its high acidity constant. The surface is ionized at low pH values and it is charged more negatively compared with other oxides [6]. At the pH value in which surface charge of diatomite is zero, Mn-diatomite

charged negatively. High negative surface charge of Mn-diatomite allows chemical adsorption.

Also, on the other way, solubility of the metal and pH of the media may be written as depending on solubility constant with the equations below. The pH value at which Co(OH)₂ begins to precipitate may be determined by simple and known formulas used by Al-Degs et al (2001) also [6].



$$\text{pH} = 14 - \log\left(\frac{\sqrt{\text{Co}^{2+}}}{\sqrt{K_{\text{sp}}}}\right) \quad (7)$$

pH value at which Co(OH)₂ begins to precipitate was calculated as 7.8 value when K_{sp} value is given as 1.3 x 10⁻¹⁵ at 20°C and maximum concentration as 25 mg/L (0.269 mM). Therefore, the studies we performed in pH intervals which surface charge of adsorbent is zero, positive and negative and at the pH threshold at which metal ion in the media will not precipitate as its hydroxide. Adsorption capacity was given as adsorption%. At the equation below,

$$\text{Adsorption \%} = \left[\frac{C_i - C_e}{C_e}\right] \times 100 \quad (8)$$

C_i is the initial concentration of the solution containing metal ion; C_e is the adsorption equilibrium concentration.

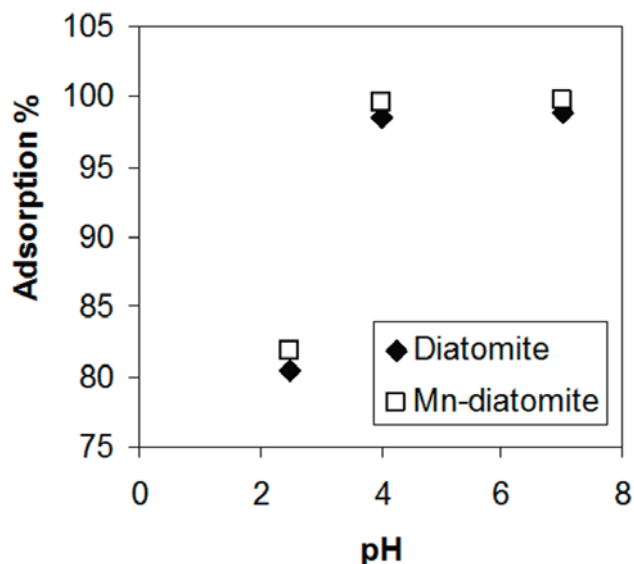


Figure 3. The effect of pH of the solution on the adsorption on diatomite and Mn-diatomite. T: 298 K, C_i : 5 mg/L.

The data at other concentration and temperature values are shown on Tables 4 and 5.

The most suitable adsorption conditions are obtained at pH values of 4 and 7 on which surface charge is zero and negative respectively. The adsorption capacity, which is 80% at pH 2.5, achieved to 99% by increasing pH. Adsorption capacity of diatomite was reached to maximum by MnO_2 modification. Variation of adsorption capacity of Mn-diatomite by pH is similar to that of natural diatomite (Table 5). While the adsorption capacity was determined as 81.95% at pH 2.5, 5 mg/L of initial concentration of Co (II) ions and 298 K, it was

99.47% at pH 4 and 99.73% at pH 7 at same temperature and concentration values.

The Effect of Concentration and Temperature on Adsorption

It was observed that the amount of adsorbed material increased by the increase of Co(II) ion concentration in the solution. Variation at pH 4 and 298 K for original and modified diatomite is given in Figure 4. Considering Tables 4 and 5, it may be seen that the amount of adsorbed material increases by the increase of Co(II) ions concentration at other temperature values (303 K, 313 K) and pH values (2.5, 7) with the help of eqn (8).

The effect of temperature on Co(II) adsorption on natural diatomite is shown in Figure 5. It was observed that the adsorption was not affected significantly within the working temperature interval (298-313 K). This allows adsorption at low temperatures. The adsorption capacity increased with modification; however, the increase in temperature did not affect the adsorption capacity. That the adsorption capacities were achieved to 98% and 99% at 298 K and pH 4 and 7 respectively for natural and Mn-diatomite shows that it is an excellent adsorbent for Co(II) adsorption at low temperatures. Diatomite and Mn-diatomite kept

Table 4. Adsorption efficiency of Co(II) ions on natural diatomite.

pH	T (K)	Adsorption %		
		A	B	C
2.5	298	80.42	80.472	82.436
2.5	303	80.71	83.035	83.005
2.5	313	80.26	82.122	81.718
4	298	98.49	97.760	94.023
4	303	98.38	98.304	94.302
4	313	98.58	97.919	93.572
7	298	98.89	99.355	99.593
7	303	99.98	99.326	99.688
7	313	99.02	99.495	99.662

Initial Co(II) concentration: (A) 5 mg/L; (B) 15 mg/L; (C) 25 mg/L.

Table 5. Adsorption efficiency of Co(II) ions on Mn-diatomite.

pH	T (K)	Adsorption %		
		A	B	C
2.5	298	81.95	84.617	84.541
2.5	303	94.88	93.871	93.012
2.5	313	95.84	94.479	93.640
4	298	99.47	99.911	99.974
4	303	99.98	99.948	99.788
4	313	99.01	99.861	99.971
7	298	99.73	99.851	99.900
7	303	98.38	99.673	99.784
7	313	99.85	99.818	99.886

Initial Co(II) concentration: (A) 5 mg/L; (B) 15 mg/L; (C) 25 mg/L.

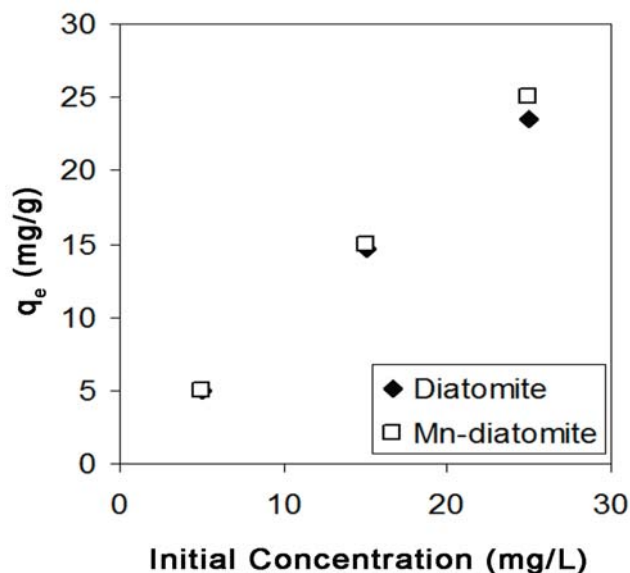


Figure 4. Variation of the amount of adsorbed material by initial metal concentration, pH: 4, T: 298 K.

these capacities when the temperature increased.

Thermodynamic Parameters of the Adsorption

Gibbs free energy ΔG , enthalpy ΔH and entropy ΔS values are very important in determining adsorption type. Since some of Langmuir constants are negative, Clasius Clapeyron equation (11) and the other equations below were used in calculating these parameters instead of Van't Hoff equation.

$$\Delta G = -RT \ln K \quad (9)$$

$$\Delta G = \Delta H - T\Delta S \quad (10)$$

$$\ln(K_2/K_1) = -(\Delta H/R) \times [(T_2 - T_1) / (T_1 \cdot T_2)] \quad (11)$$

K is equilibrium constant calculated from Langmuir adsorption isotherm; T is absolute temperature (K) and R is universal gas constant (J/mol.K). Thermodynamic quantities calculated for diatomite and Mn-diatomite are seen in Tables 6 and 7.

As seen on Tables 6 and 7, that ΔH , one of the thermodynamic parameters, for the adsorption of Co(II) ions on original diatomite is negative indicates the process is exothermic. That the value of ΔH_{ads} is lower than 40 kJ/mol indicates that the adsorption

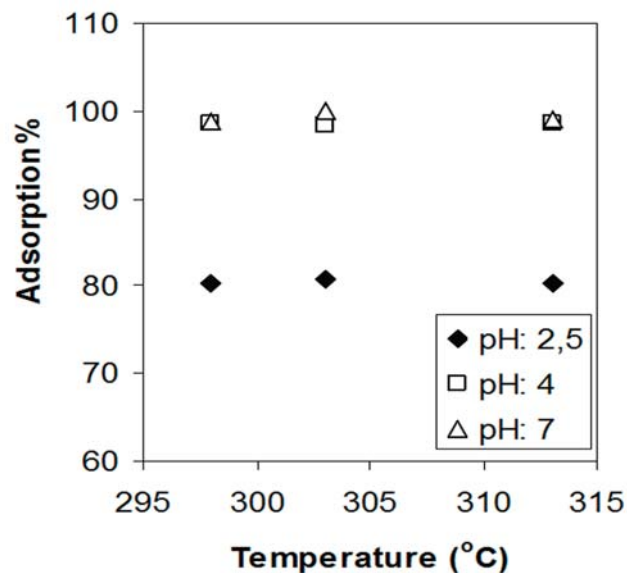


Figure 5. The effect of temperature on the adsorption for natural diatomite, $C_i = 5$ mg/L.

is physical. Positive ΔS values indicate that the irregularity increased on the interface between Co(II) ions solution and original diatomite during the adsorption. Generally positive ΔH values indicate that the adsorption of Co(II) ions on modified diatomite is endothermic. That the value of ΔH_{ads} is higher than 40 kJ mol⁻¹ indicates that the adsorption is chemical. Negative ΔS values indicate that the irregularity decreased on the interface between Co(II) ion solution and modified diatomite during the adsorption. Negative Gibbs free enthalpy values, ΔG , for the original and modified diatomite indicates that the adsorption occurred spontaneously. When the adsorption energies are compared, it is seen that ΔH values are higher. However, the entropy is lower than Gibbs free enthalpy. Therefore, it may be

Table 6. Some thermodynamic parameters calculated for the adsorption of Co(II) ions on original diatomite.

pH	T(K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol.K)
2.5	298	-	-	-
4	298	-16.9482	42.5048	0.1995
7	298	-	-	-
2.5	303	-16.3589	-	-
4	303	-16.5194	-23.6737	-0.0236
7	303	-18.4594	-	-
2.5	313	-	-31.1700	-
4	313	-17.846	-0.8861	0.0541
7	313	-	-16.2366	-

Table 7. Some thermodynamic parameters calculated for the adsorption of Co(II) ions on Mn-diatomite.

pH	T(K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol·K)
2.5	298	-	-	-
4	298	-21.6308	245.6687	0.8969
7	298	-	-	-
2.5	303	-15.3777	-21.8537	-0.0213
4	303	-17.8718	-115.7526	-0.3230
7	303	-23.7990	580.7788	1.9953
2.5	313	-16.6064	-	-
4	313	-22.2819	8.6971	0.0989
7	313	-5.4169	-	-

said that the adsorption of Co(II) on original and modified diatomites are enthalpic governed. That the adsorption is performed by ΔH explains that the reaction occurs spontaneously.

CONCLUSION

The diatomite from Çaldıran/Van, which is a local raw material, is a good adsorbent for Co(II) ion adsorption from aqueous solution. The adsorption reaches to maximum at pH 4 and 7. These pH values are the values at which surface charge of the

diatomite is zero and negative. The adsorption capacity was determined as 98% for original diatomite at 298 K and for Co(II) solutions with 5 mg/L initial concentration at pH 4 and 7. Because the adsorption capacity is high, the adsorbent may be used in its natural form without needing modification for Co(II). After modification of diatomite with MnO_2 , adsorption capacity is 99.47% and 99.73% respectively for the given pH values at the same temperature and metal ion concentration. Co(II) ions adsorption capacity of the diatomite, which its surface was made more negative by MnO_2 , was increased. Langmuir and Freundlich models were applied from adsorption isotherms and it was determined that the adsorption correlates with Langmuir adsorption isotherm depending on R^2 values. Therefore, we may say that Co(II) ions are adsorbed with maximum capacity as monomolecular on the surface of diatomite and Mn-diatomite. According to adsorption free enthalpy (ΔG) and adsorption enthalpy (ΔH) values, the adsorption of Co(II) ion on the original diatomite is physical adsorption and occurs spontaneously. However, the adsorption of Co(II) ion on Mn-diatomite is chemical adsorption and occurs spontaneously.

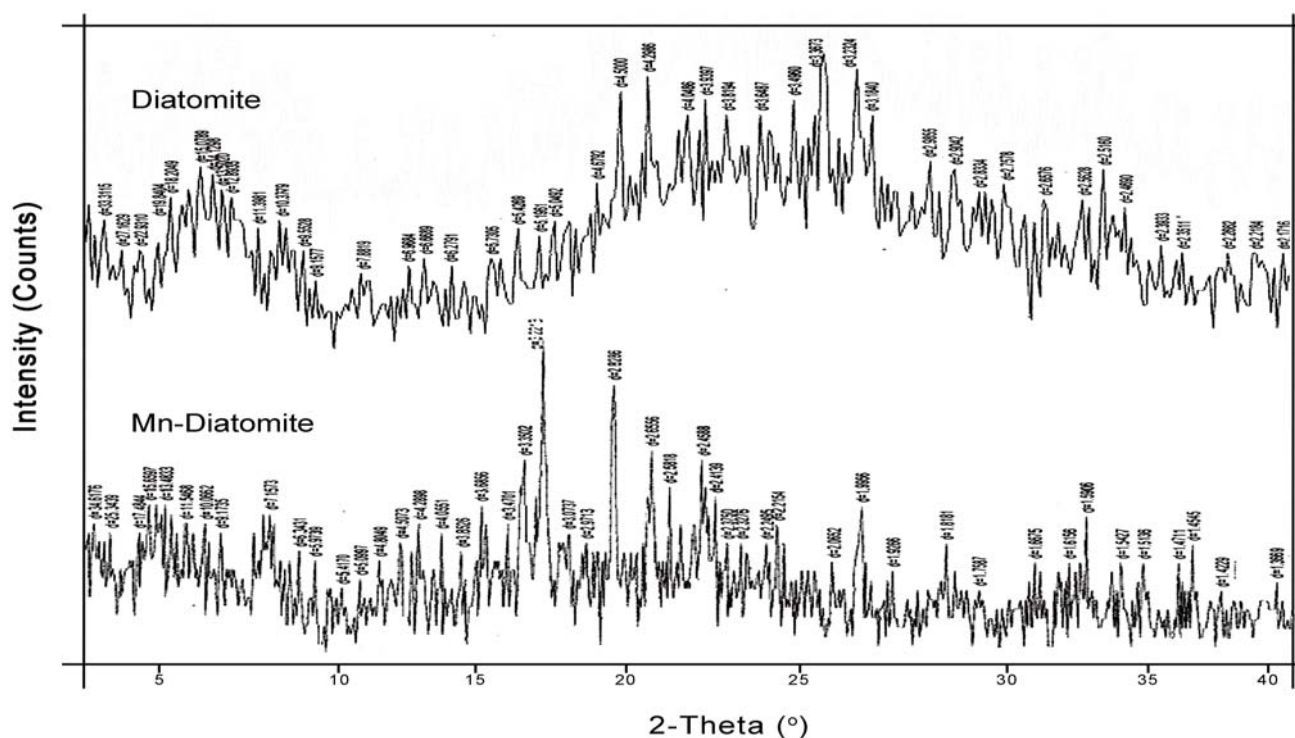


Figure 6. XRD spectra of natural and modified diatomite.

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